

REINHOLD PLASTICS APPLICATIONS SERIES

PHENOLIC RESINS

by

DAVID F. GOULD

The Borden Chemical Company

A Division of The Borden Company

**REINHOLD PUBLISHING CORPORATION
NEW YORK
CHAPMAN & HALL, LTD., LONDON**

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Library of Congress Catalog Card Number: 59-13265

Printed in the United States of America

Reinhold Plastics Applications Series

This book is the eleventh of a series started in 1957 with the publication of Theodore Kresser's book on polyethylene. The theme of the series is guidance in application. The optimum application of a plastic in a very real sense determines its true worth. Most of the books in the series describe the properties, the chemistry and the applications of a single plastic or of a single family of plastics. A few describe fabrications of plastics.

Those already published are the volumes on polyethylene, polyurethanes, polyamide resins, plastic sheet forming, cellulosics, vinyl resins, fluorocarbons, epoxy resins, gum plastics, and laminated plastics. Those in preparation include the following: acrylic resins, amino resins, polystyrene, silicones, polyesters, and cast plastics.

The series is semi-technical—that is, one does not need to be a research chemist to understand the various volumes. The authors have kept in mind as probable readers such industrial men and women as design engineers, equipment manufacturers, producers of packages, manufacturers of packaging machinery, students at technical schools and, of course, all people in the plastics industry—material manufacturers, molders, extruders, fabricators.

In addition to the above, it is hoped that each title will appeal to readers in specialized categories. Plastics from which fibers are made may be of interest to tire and fabric manufacturers. One book, for instance, may describe materials favorable for production of sheets used for handbags

and luggage. Similarly, other titles may appeal to manufacturers of paints, magnetic tapes, upholstery, plywood and furniture.

With the series now about half complete, and with encouragement from its wide acceptance in industry, it is with enthusiasm that this eleventh book is presented.

HERBERT R. SIMONDS, *Editor*

Titles Published

Cellulosics, *Walter Paist*

Epoxy Resins, *Irving Skeist*

Fluorocarbons, *Merritt A. Rudner*

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PREFACE

If we had had no phenolic resins heretofore, the introduction of resins with the properties of the best phenolics of today in all probability would be sensational. The promotion of many new and perhaps more glamorous resins has undoubtedly made it difficult for many to realize that this "workhorse of the plastic industry" is doing more than just plodding along. It is a most versatile type of resin that plays an important role in modern industry.

It is hoped that this book will give to the architect, the designer, the engineer, and the business man a better conception of the possibilities of phenolics; to the resin manufacturer and user information that may lead to better phenolics and even more effective use; to the laboratory man a refresher course on the practical aspects; and to the student a survey of an important industry.

Discussion of the chemistry and reaction mechanisms of these resins has been held to a minimum but not from lack of appreciation of their importance. Disclosures in patents and elsewhere have been selected frequently to illustrate trends of thinking in the development of resins, processes, or applications. It is hoped that they may encourage new ideas for further improvements and expansions.

Sincere thanks are offered to the companies which supplied information or illustrations, to the publications which granted reproduction of their material, and to the numerous individuals who helped with criticisms and suggestions. The

encouragement of executives of The Borden Chemical Company is deeply appreciated. Finally but not least, my thanks to my wife Marjorie for her aid and helpful criticism and to Marian Burke Gould for efficiently typing the manuscript.

DAVID F. GOULD

Burlington, N. J.
July, 1959

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1. PRESENT STATUS OF PHENOLIC RESINS

The term “phenolic resins” designates what is probably the most varied and versatile group of synthetic resins that we have. These resins are also known as “tar-acid resins.” Tar acids or phenols recovered from coal tar distillates have always been important raw materials for the production of these resins.

Phenols are characterized by the presence of an hydroxyl group attached to a benzene ring. Most of current phenolic resin production is made by the condensation of a phenol with formaldehyde, but there are many phenols and many chemicals other than formaldehyde that form resins with phenols. The properties of the resins made from the various combinations will vary widely with the selection and proportions of reactants.

Another important factor in determining the properties of the resin is the type of chemical structure that the reactants form as they combine. This is controlled primarily by the choice of the catalyst or the combination of catalysts used to activate the condensation reaction.

Temperature and the order of addition of the reactants also affect the results. Various modifying agents may be added before, during, or after the condensation. Not nearly enough is known about the reactions involved to take full advantage of their possibilities.

There are limits to the extent to which the properties of phenolic resins may be modified. Nevertheless, the range of choice of materials and methods gives one wide latitude for building a resin to meet a specific application requirement.

Extent of Use

The extensiveness of applications of phenolic resins has led to their being referred to as the “workhorse” of the plastic industry. They first appeared commercially in 1909 and are exceeded in age among the synthetic plastics only by cellulose nitrate (Celluloid). Phenolic resins have been pioneers in many applications and still maintain a commercial position in most of them, in spite of the advent of new types of resins.

Increasingly stringent performance demands in most fields of use, the development of new applications, and the competitive effect of new resins have acted as continuous incentives of technical development of phenolic resins. Those of today are far removed in quality and performance from the phenolic resins of nearly 50 years ago. However, there is still plenty of opportunity for improvement. In recent years, increased attention has been given to the fundamentals of the condensation reactions and to the establishment of relationships between resin structure and resin properties, all of which is in the right direction.

Trend of Interest

A rather interesting index of the amount and trend of technical interest in these resins is provided by the number of references cited annually in *Chemical Abstracts* under the heading "Phenol Condensation Products." These have been plotted as shown on Figure 1.1. Two dips may be noted in the number of citations in the vicinity of 1920 and 1944, respectively. They probably reflect a delaying effect on publications due to wartime conditions.

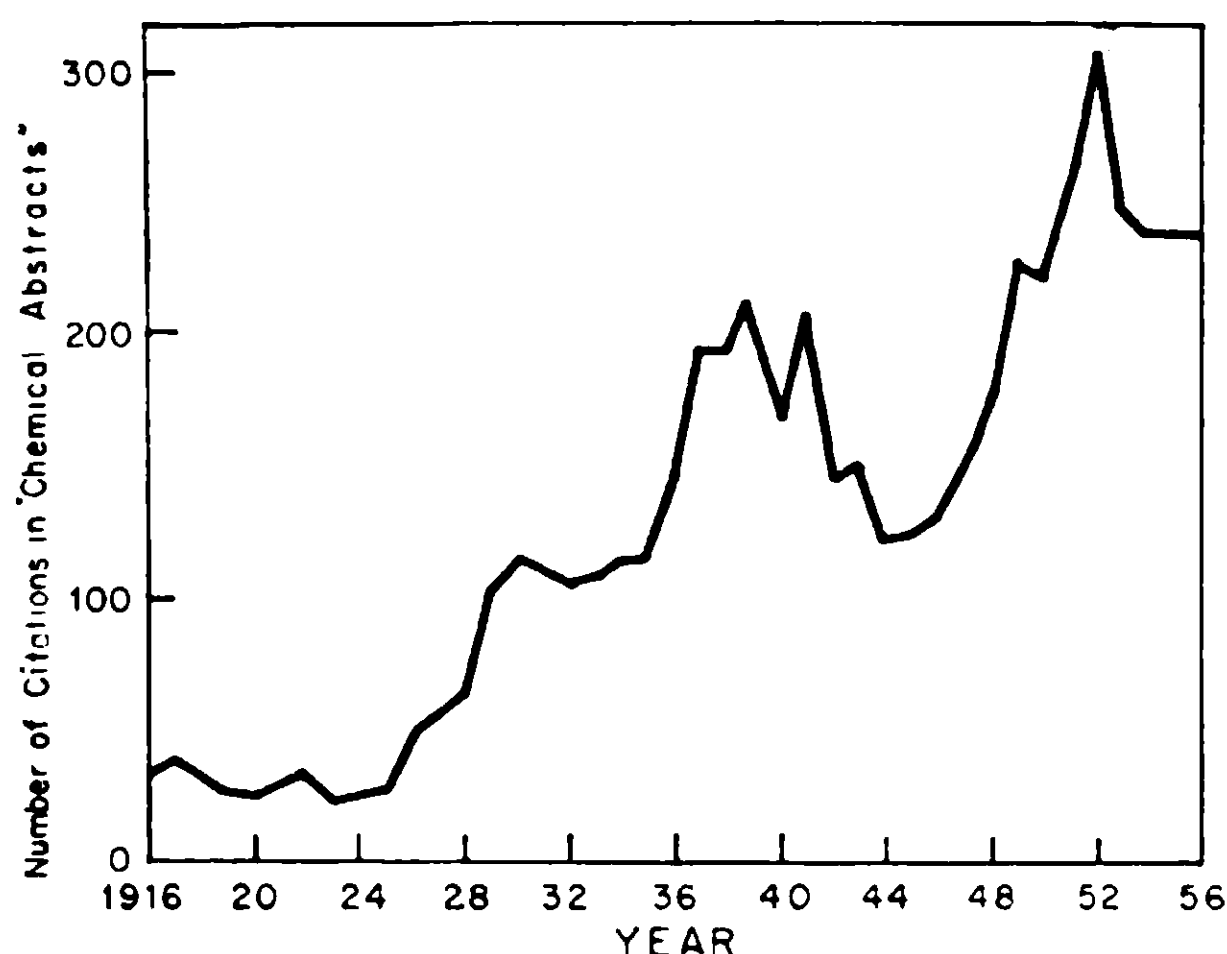


Figure 1.1. Phenolic condensation products.

Production

Phenolic resins have become so well established in industry that their annual production rate follows quite closely the ups and downs of the Federal Reserve Board Index for all industrial production, as will be noted on Figure 1.2. The production of phenolic resins in 1957 was about $1\frac{1}{2}$ times the production in 1947 and 5 times the production in 1937. In 1956, the production of phenolic

resins for the major classes of use was approximately as follows:

Bonding and adhesive resins	239 million lb
Molding resins	113
Protective coating resins	28
Other resins	45
	425

These data are based on U.S. Tariff Commission statistics with deduction for filler in molding compound as reported by that agency.

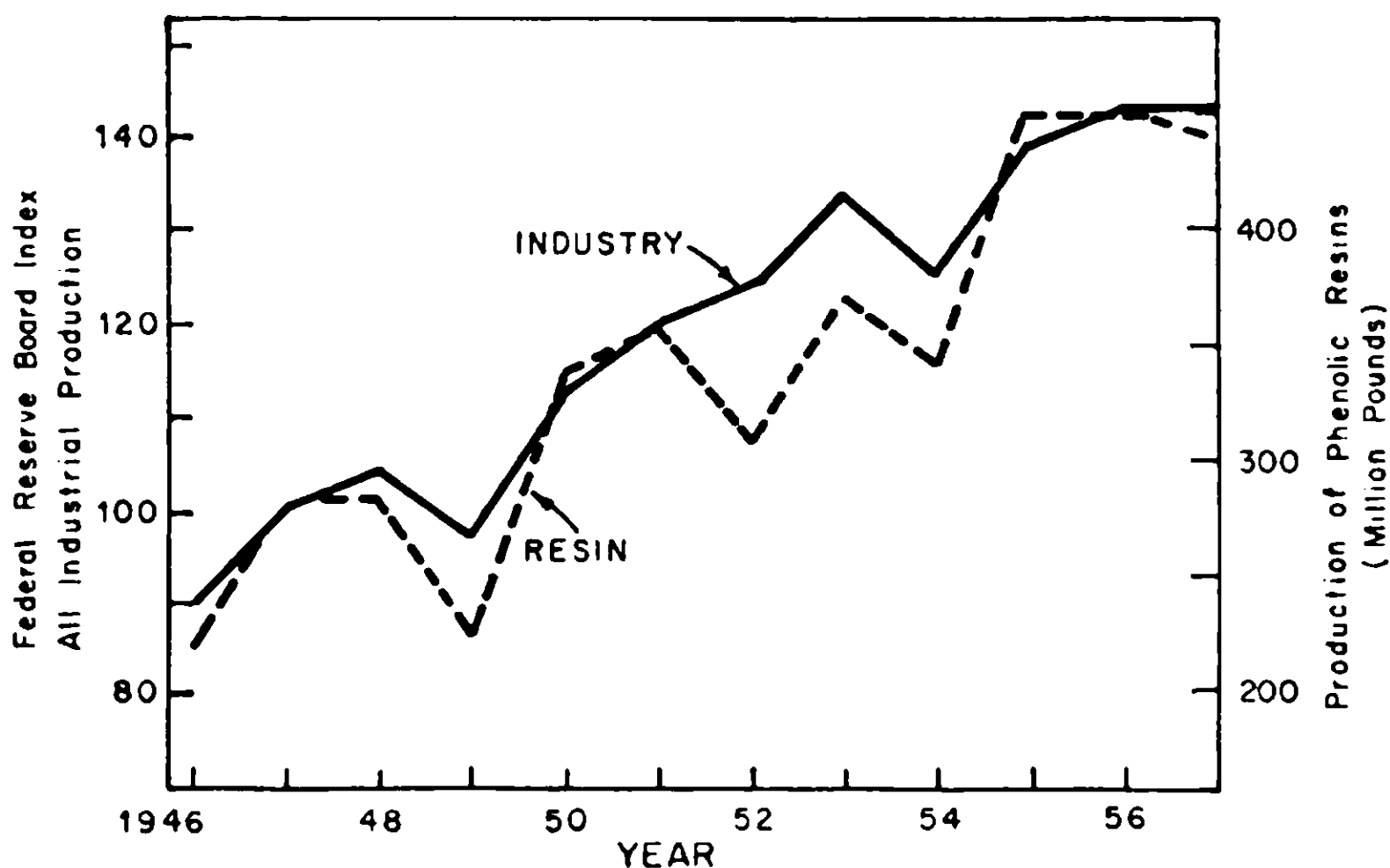


Figure 1.2. Phenolic resin production versus all industrial production.

Thermosetting Resins

Most phenolic resins are of the thermosetting type. The condensation reaction, by which they are formed, is generally carried to a stage at which the resins are workable for the intended application. After the resins have been spread, shaped, or otherwise processed, the reaction is usually caused to continue under suitable conditions until the resins are converted into insoluble and infusible prod-

ucts. This hardening or cure is essential to the development of the best physical properties of the resin in most applications and constitutes one of their most valuable features. At the same time, this characteristic also limits the applicability of the resins to some extent.

Competitive Resins

The principal *thermosetting resins* competitive with phenolic resins are the urea-melamine group, most polyesters, the alkyds, and the epoxy resins. Production and average unit value data for these resins are shown in Table 1.1. Epoxy resins might be classified as phenolic resins on the basis of the raw materials from which they are derived. However, their properties and their growing industrial importance warrant separate treatment, and they are not considered in detail here.

The commercially important class of *thermoplastic resins* is distinguished by the ability of these resins to be repeatedly softened by heating and hardened by cooling, without converting to an infusible and insoluble stage. Production and average unit value for three important representatives of this class of resins are shown in Table 1.1 for comparison. They are currently competitive with phenolic resins in restricted fields only.

There are some applications, such as the production of tough flexible sheets, rods, or tubes or the molding of formed parts of high clarity, for which thermoplastic resins are suited and phenolic resins are not. Current types of thermoplastic resins soften at temperatures sufficiently low as to prevent to a large extent the use of these resins in some fields of application now served by phenolics and other thermosetting resins. The heat distortion temperature is higher in some of the newer thermoplastic resins, and

TABLE 1.1. RESIN PRODUCTION AND AVERAGE UNIT VALUE
OF RESIN (1956)*

	Millions of lb	Cents per lb
Thermosetting Resins		
Phenolic resins	450	26
Alkyds	473	31
Urea resins	225	23
Melamine and melamine-urea resins	96	47
Polyesters	99	41
Epoxy resins	36	67
Thermoplastic Resins		
Styrene resins (other than alkyd)	659	31
Polyethylene	565	37
Vinyl resins	759	34

Phenolic Resins

	Cents per lb
1950	23
1951	27
1952	27
1953	27
1954	—
1955	27
1956	26

* Source: U.S. Tariff Commission, corrected for fillers in phenolic and urea molding resins.

with each such increase the competition that phenolic resins must meet, particularly in the production of molded parts, becomes more severe.

Prices

As is to be expected in the case of a product so long established and with strong competition, prices of the common grades of phenolic resins have been forced down

to a practical minimum. Captive production of the major raw materials, phenol and formaldehyde, has helped some of the manufacturers of these types of phenolics. On the other hand, new types of phenolic resins are selling in the dollars per pound bracket. These have not yet developed into large volume production but they have good potentialities.

2. RAW MATERIALS

Phenol or hydroxybenzene is the fundamental unit from which the others may be considered to be derived. The derivatives range from simple ones with a $-\text{CH}_3$ group attached to the benzene ring to complex compounds with several types of substituent groups. In descending order of importance from the standpoint of resin production are the following classes of phenols: (*a*) monohydric phenols, (*b*) polyhydric phenols, (*c*) complex phenols, and (*d*) polynuclear monohydric phenols.

The monohydric phenols are further divided into several subclasses, which cover a wide range of properties.

MONOHYDRIC PHENOLS

Phenol

Approximately three-quarters of current phenolic resin production is derived from phenol itself. Its availability and a relatively high and uniform purity, which facilitates

control of the condensation reaction in resin manufacture, are valid reasons for this. In 1956, synthetic resins consumed approximately 66% of the phenol produced.

In the past, phenol was obtained commercially from coal-tar distillates only. A substantial amount is still produced from that source. A smaller amount is obtained from petroleum operations. Phenol also occurs in a variety of other materials, but the amounts contained therein are too small to be of practical significance. These so-called natural sources long ago proved inadequate for the needs of the chemical industry, and industry turned to synthetic methods. According to the U.S. Tariff Commission, 93% of the phenol produced in 1956 was synthetic.

Synthesis and Commercial Production. There are a great many ways in which phenol may be synthesized, but only a few of them have been able to reach the commercial stage. All the synthetic processes of commercial importance at present start with benzene. In the past, benzene was also derived exclusively from coal tar. In 1956, one-third of the benzene produced in this country came from petroleum.

As to methods of synthesis, direct oxidation of benzene by air or oxygen has an apparent simplicity that has attracted a great deal of experimental attention to the process. The basic reaction is:



This reaction occurs, but the phenol oxidizes even more readily than the benzene, and the net result is a lot of by-product and little phenol. The process has been in pilot-plant operation but cannot compete with present commercial processes.

In 1952 a Government committee predicted phenol production of 1350 million lb in 1975 from the hydrogenation of coal. The only current production is from a pilot unit

with a reported capacity of about 3 million lb per year. The phenol is only one of a long series of co-products that must be disposed of economically.

There are four processes for the synthesis of phenol in use today. The distinguishing characteristics are summarized below; it will be understood that there may be recirculation of reagents, secondary reactions, or other features that complicate each process.

1. *Sulfonation-fusion process*: Benzene is sulfonated and the product is fused with caustic soda to form sodium phenate, from which phenol is liberated by acidifying. This is the oldest commercial process.
2. *Chlorobenzene (caustic) process*: Benzene is chlorinated to the monochlorobenzene, which is then hydrolyzed at high temperatures and pressures to sodium phenate. Phenol is recovered after acidifying. Probably more phenol is produced by this process than any other.
3. *Chlorobenzene (Raschig) process*: Benzene is converted into monochlorobenzene in a vapor phase, catalytic reaction. The monochlorobenzene is subsequently hydrolyzed to phenol in another vapor phase, catalytic reaction.
4. *Cumene process*: Benzene is alkylated to isopropylbenzene in a catalytic process. The isopropylbenzene is oxidized to its hydroperoxide, which is in turn hydrolyzed to phenol and acetone. About 0.6 lb of acetone is produced per pound of phenol. This is a relatively new process and it has attracted much attention. By substituting appropriate hydrocarbons for the cumene, other mono- and dihydric phenols may be produced. *Para*-cresol production is commercial and production of resorcinol and hydroquinone has been demonstrated.

Based on several published estimates of plant capacities and on U.S. Tariff Commission statistics, the production of phenol in this country in 1956 is estimated to have been distributed according to process as indicated in Table 2.1.

TABLE 2.1. PHENOL PRODUCTION

Synthetic Products

Chlorobenzene (caustic) process	32%	
Sulfonation-fusion process	23	
Chlorobenzene (Raschig) process	21	
Cumene process	17	
		93%

Natural Products

From coal tar operations	6	
From petroleum operations	1	
		7
		100%

A substantial amount of equipment is required for commercial production of phenol. Minimum economical plant capacity varies with the process but is generally at least 15 million pounds per year. At 1958 prices, plant investment cost would probably average about \$600 per ton per year capacity.

Published estimates of production costs of phenol vary rather widely. Costs by the three older processes are probably reasonably close to one another and cost by the cumene process possibly may be a cent a pound less. There is more chance for fluctuation in cost by the cumene process, due to the effect of the market for acetone.

The quality of the phenol from each of the four processes is high. Chlorine and sulfur are the principal impurities and they generally occur in amounts of only a few thousandths of a per cent. Brief work in the author's and other

laboratories suggests that phenol from the sulfonation-fusion process might be slightly faster in reaction with formaldehyde. It is possible that specific sulfur compounds from the sulfonation-fusion process may act as reaction accelerators. Any present differences are easily corrected by an adjustment in the amount of catalyst.

The bulk of the phenol used for phenolic resins is classified as the U.S.P. grade, although much of the commercial material exceeds the requirements of the U.S. Pharmacopoeia in some respects. The usual properties of U.S.P. phenol used for resins are as follows:

Appearance	White, crystalline
Congealing or freezing point	40.6°C. minimum
Solution in water (5 ml in 75 ml)	Clear
Specific gravity, liquid, 50°/15.5°C.	1.05
Odor	Characteristic, free of sulfury or other foreign odors.

In some instances, 90% or 82% phenol may be specified for the production of special resins. Their characteristics are:

	90%	82%
Specific gravity, 50°/15.5°C.	1.048	1.045
Freezing point, °C.	36–37	30.5–32

Cresols make up the balance of these two phenols and give desired properties to the resins made with them.

Alkyl Phenols

The principal alkyl phenols are shown in Table 2.2. Not all of them are useful in phenolic resins. As will be discussed later, they are selected according to their resin-forming properties.

Sources. The bulk of the alkyl phenols with short side chains are derived from tar produced as a by-product of coke production at steel mills. Distillates from the tar are extracted with caustic soda solution, the extract is treated to remove impurities and is then acidified to liberate the tar acids or phenols. The tar acids are mixtures of the phenols shown in Table 2.2, the composition varying with the type of coal used in the coke oven, the coking cycle, and other factors.

TABLE 2.2. TAR ACID COMPOSITION*

Coking	1951 Normal	1953 Slow
<i>Composition of the tar acid</i>		
Phenol	34.5%	29.0%
<i>Ortho</i> -cresol	9.0	9.5
<i>Meta</i> - and <i>para</i> -cresols	27.5	31.5
Low-boiling xylenols	6.5	8.0
High-boiling xylenols	9.0	10.5
Higher-boiling acids, residue	13.5	11.5
	<u>100.0</u>	<u>100.0</u>

* *Chemicals and Rubber*, Mar. 1957.

Coking at steel mills in this country is classified as high temperature coking. The composition of typical tar acids from such operations is given in Table 2.3 for two periods to show the effect of slowing down the coking operation, as when the demand for coke drops. Slowing the operation means coking at lower temperature.

Low Temperature Coking. Coking of coal at temperatures lower than those that usually prevail in the ovens at steel mills has been promoted at various times. The tar acids from such operations have a lower content of phenol

itself. Fractions in the cresylic acid range form resins that cure more slowly than resins made from high-temperature tar acids of the same boiling range. The difference is probably due principally to a greater complexity of the hydrocarbon side groups in the phenols from low temperature tar acids.

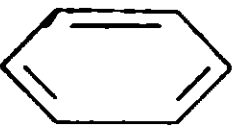
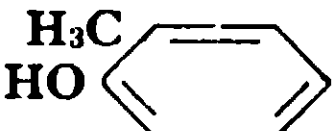
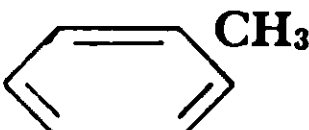
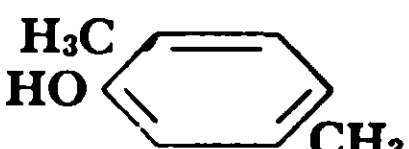
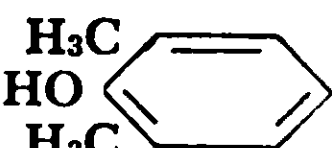
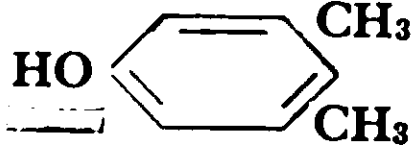
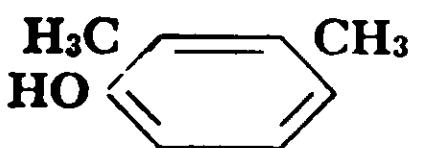
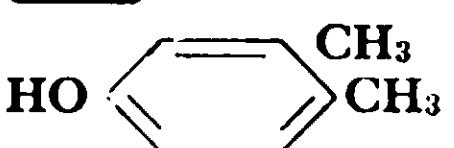
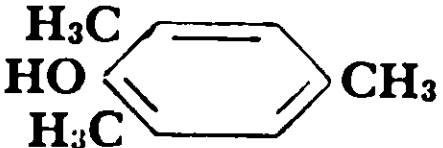
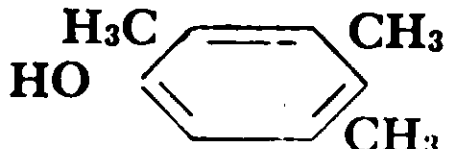
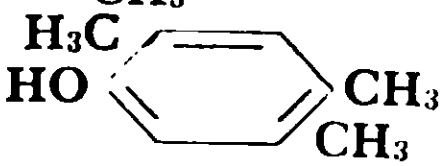
Petroleum Acids. Another source of phenols is cracked petroleum distillates. Samples of acids from that source yielded cresylic acid fractions that reacted even more slowly than similar fractions from low temperature tar acids. Such acids are not important as raw materials for resins.

Tar Acid Production. Crude tar acids are commonly separated by means of a series of column distillations into a number of fractions boiling in the phenol, cresol, xlenol, and cresylic acid ranges respectively. The fractions may be used as such or they may be processed further. Methods are available for isolating phenol and a few other individuals in relatively pure form when required.

Use of Fractions. A single fraction or a combination of fractions from the distillation of the tar acids is used as needed to get the properties desired. Fractions are selected on the basis of their resin-forming characteristics. One fraction may make a faster curing resin, another may make a resin having better solubility in oils, another may make a resin with exceptional bonding properties. Still others are eliminated as being unsatisfactory for resin production.

Each fraction commonly contains phenols of various degrees of reactivity with formaldehyde. In practice, the condensation reaction is usually carried out in a manner that draws the less reactive component into the resin molecule along with the more reactive components. If desired, it is possible to condense the more reactive phenol and leave the unreactive phenol essentially unchanged.

TABLE 2.3. ALKYL PHENOLS

	Structure	Boil. Pt. °C.	Melt. Pt. °C.
Phenol	HO 	181	41
Cresols			
<i>Ortho</i>		191	31
<i>Meta</i>	HO 	213	12
<i>Para</i>	HO 	202	35
Xylenols			
1, 2, 4		211	26
1, 2, 5		211	74
1, 2, 6		212	49
1, 3, 5	HO 	219	68
1, 2, 3		218	75
1, 3, 4	HO 	225	65
Trimethyl phenols			
1, 2, 4, 6		219	68
1, 2, 3, 5		230-1	95
1, 2, 4, 5		235	72

Synthesis. Alkyl phenols may be synthesized by the methods used for phenol but using as raw material the appropriate alkyl benzene. Another method of synthesis is the replacement of the *ortho* or *para*-hydrogen in phenol by aliphatic groups in a simple catalyzed reaction.

A few synthesized alkyl phenols are important in phenolic resin production. They include *para-tert*-amyl phenol, *para-tert*-butyl phenol, octyl phenol, and nonyl phenol. Their major use is in oil soluble resins for surface coatings of various types, where the long aliphatic side chains of the phenols aid the oil solubility of the resin. Phenols with even longer side chains are being studied.

Aryl Phenols

The only representative of this group that is now of significance in the phenolic resin industry is *para*-phenylphenol or *para*-hydroxybiphenyl. It is used in the manufacture of oil-soluble resins which are suited for insulation and marine paints.

Alkenyl Phenols

The preparation of resins from this type of phenol is relatively new and not thoroughly explored. Results already obtained appear to warrant further study in spite of present high cost. A series of British patents granted in 1953 discloses the preparation and use of polymers and copolymers of vinyl phenol.⁶ In some cases colorless resins were obtained. The resins are said to be useful in adhesives, lacquers, and molding materials. The production of resins from formaldehyde and *para*-, *ortho*-, 1,5-di-, 1,3-di-, and 1,3,5-tributenyl phenols has been disclosed.⁷ Propenyl phenol and others have also been studied.

Phenols with Substituent Groups on the Ring other than C-H

Chlorinated Phenols. Chlorinated phenols are of particular interest as means of introducing fire-retardant properties into phenolic resins. According to Soule⁸, condensation products of phenol-dichlorophenol mixtures are less viscous than straight phenol-condensation products, which is a distinct advantage where impregnation with resin is involved. He also points out that they cure under milder conditions. Burke and co-workers⁹ have discussed the use of chlorophenols to form linear polymers with formaldehyde and the dehalogenation of those polymers to high-molecular weight linear phenol-formaldehyde polymers. At present, *para*-chlorophenol and dichlorophenols appear to be the raw materials of most interest.

Sulfonated Phenols. Phenols may be sulfonated more easily than the benzene hydrocarbons. Various sulfonated phenols have been condensed with formaldehyde, mostly for the production of tanning agents and ion exchange resins. In some instances, other materials are added to the phenol before sulfonating it. Thus Petrov and associates¹⁰ sulfonate a mixture of castor oil, phenol, and turpentine and then condense the product with an aldehyde to form a water-soluble resin.

Esters. Various proposals have been made to esterify phenols and then condense with formaldehyde. The intent has been to introduce novel properties into the resin, but apparently none have any extensive application at present.

Phenols Converted into Intermediates Reactive with Formaldehyde

In order to get resins of improved thermal stability, Moorhead¹⁶ reacts a siloxane and a monohydric or dihydric

phenol and then condenses the product with an aldehyde. Evans and Whitney⁶ prepare copolymers of vinyl phenol with styrene, acrylic compounds, vinyl esters or ethers, or allyl monomers. The copolymer is then condensed with an aldehyde in the presence of a condensation catalyst to form resins that thermoset and are resistant to acids, alkalis, solvents, and water.

Polynuclear Monohydric Phenols

There are phenols in the naphthalene and the anthracene families of chemical compounds. The most important phenols allied to naphthalene are alpha- and beta-naphthol. Both form resins with formaldehyde. The resin from beta-naphthol can be made oil-soluble by heat treatment. Resins useful in varnishes and polishes have been prepared from alpha-naphthol.

There are no indications that naphthols have advantages that will make them important in phenolic resins in the foreseeable future.

The phenols allied to anthracene are also not of significance in the production of phenolic resins. Production of phenolic resins using the anthracene portion of coal-tar distillates has been proposed. Judging by the complexity of that raw material, it would seem unlikely that resins of superior or uniform quality would be produced.

POLYHYDRIC PHENOLS

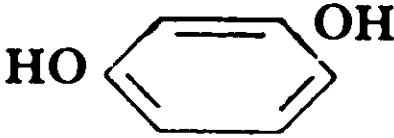
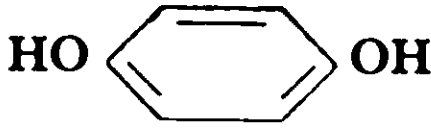
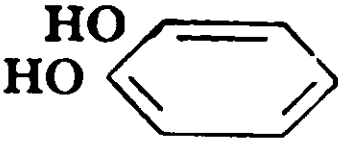
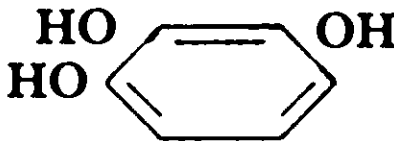
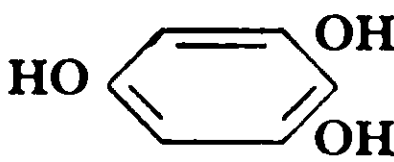
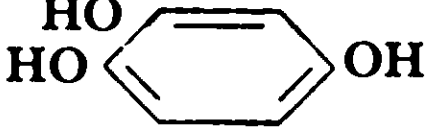
Dihydric Phenols

Of the three dihydric phenols, resorcinol, hydroquinone, and catechol, only resorcinol is at present commercially

important in resin manufacture (see Table 2.4). Hydroquinone has been studied experimentally, but apparently the resins have no outstanding properties. Kropa and Welcher¹⁵ disclose some interesting reversible oxidizable and reducible resins obtained by condensing hydroquinone and a phenol having no substituents in the *ortho* or *para* positions with an aldehyde.

Judging from the patents that have appeared in recent years, attention to catechol as a resin-forming material has been confined largely to Germany. Resins from catechol-formaldehyde condensation product, and the use of catechol-containing fractions from the products of the hydrogenation of brown coal are subjects of recent disclosure.

TABLE 2.4. POLYHYDRIC PHENOLS

	Structure	Boil. Pt. °C.	Melt. Pt. °C.
Resorcinol		276	110
Hydroquinone		286	170
Pyrocatechol		240	105
Pyrogallol		309	133-4
Phloroglucinol			219
Benzenetriol (1, 2, 4)			140

Resorcinol produces excellent, fast-curing resins and would probably find more extensive use if the price were lower. For some years the sales price of resorcinol has

been 4 to 5 times that of phenol. As a result, about three-quarters of the resorcinol that goes into resins is used in combination with phenol as a compromise between cost and performance.

The usual process for the manufacture of resorcinol is a modification of the sulfonation-fusion process for phenol, the main difference being that here the sulfonation is carried further to form the disulfonic acid. Side reactions that may occur and the nature of the materials handled make the process considerably more complicated than in the case of phenol. Resorcinol may be made by an adaptation of the cumene process for phenol. Whether that will have an appreciable effect on the price and availability of resorcinol remains to be demonstrated.

Trihydric Phenols

Price and restricted supply have kept the trihydric phenols from becoming important in the resin industry. There are no indications of any change in this in the immediate future.

Complex Phenols

In the search for cheaper dihydric phenols, considerable attention has been given to natural tannin materials, which contain phenolic materials. Knowles and White¹¹ have reported on a study of quebracho and mimosa tanning extracts. These extracts contain structurally complex units of resorcinol or phloroglucinol connected to catechol or pyrogallol nuclei. They have been studied as raw materials for condensation with formaldehyde and as catalysts for other resin-forming reactions and especially the phenol-formaldehyde reaction. The latter application is reported

to be in commercial use by adhesive manufacturers in England. The delivered price there is apparently more favorable in comparison with that of phenol than is the case in this country.

Gum accroides contains phenolic tannols and has been used to some extent in the past, particularly in combination with phenol-formaldehyde condensation products. Its use has declined, probably because results obtained with it were not sufficiently reliable, as is frequently the case with natural products.

Another plant derivative containing phenolic bodies is the oil contained in the fruit of the cashew tree which is roasted out before the nuts are extracted. The crude cashew nutshell liquid is very irritating to the skin, and the oil is treated before use to minimize this effect. On distillation, a very high-boiling phenolic mixture is obtained. This mixture, known as cardanol, is composed of 90% *meta*-substituted phenols with various degrees of unsaturation in a 15-carbon side chain and about 10% of *meta*-substituted resorcinol having a 15-carbon side chain. In some cases the cardanol is hydrogenated and derivatives prepared. In its various forms this material finds use in insulating varnishes, resins for frictional elements, resins for rubber modification, and resins for laminating.

Polyphenols

Commercially, the most important representative of this group is 2,2'-bis (hydroxyphenyl)-propane or Bisphenol-A. This material is made by the reaction of phenol and acetone under acidic conditions. Similar products may be made by substituting other ketones for the acetone. United States Tariff Commission data indicate that over 4 million lb of formaldehyde-condensation products were made from this

phenol in 1956. In addition, a large part of the 34 million lb of epoxy resins made that year was also derived from it.

Other polyphenols have been studied, and some of them appear to offer opportunity for resin cost reduction. Farnham¹² reacts phenol with an olefinic aldehyde, such as acrolein, under acidic conditions. The products are relatively low-molecular weight materials and condense with formaldehyde to form phenolic resins. New methods of production are giving an increased importance to acrolein, and reactions of this type may be more common in the future.

Hermann,^{13,14} in a series of patents, discloses the production of polyphenols, having 2 to 3 phenolic nuclei joined by a chain of 5 to 9 atoms, by reaction of a phenol with an unsaturated fatty acid. Other unsaturated materials, such as styrene or vinyl acetate, may also be present.

These polyphenols may be condensed with formaldehyde to form resins of high elasticity and film-forming properties. Phenols also condense with vinyl ethers, such as butanediol divinyl ether, in the presence of alkaline catalysts to give products with two hydroxyphenyl groups per molecule.

SELECTION OF PHENOLS FOR RESINS

In general, the highly reactive phenols form condensation products that cure rapidly to hard insoluble resins, while phenols of low reactivity form condensation products that show little or no tendency to harden. The major structural feature of a phenol that determines its reactivity with aldehydes is its functionality. This may be defined as the total number of unsubstituted positions on the benzene ring that are in *ortho* or *para* position to the hydroxyl group.

The connection between functionality and resin formation for some of the common phenols is shown in Table 2.5.

TABLE 2.5. PHENOL FUNCTIONALITY

Function- ality	Type of Phenol	Reactivity with Formaldehyde	Nature of Conden- sation Product
0	2,4,6-Trialkyl	Nil	—
1	1,2,4-Xylenol	Very slow	Low-molecular wt.
	1,2,6-Xylenol	Very slow	Low-molecular wt.
2	<i>p</i> -Cresol	Slow	Uncurable to diffi- culty curable
	1,2,3-Xylenol	Slow	Uncurable to diffi- culty curable
	1,2,5-Xylenol	Slow	Uncurable to diffi- culty curable
	1,3,4-Xylenol	Slow	Uncurable to diffi- culty curable
3	Phenol	Rapid	Highly curable
	<i>m</i> -Cresol	Rapid	Highly curable
	1,3,5-Xylenol	Rapid	Highly curable
	Resorcinol	Rapid	Highly curable
4	Hydroquinone	Rapid	Highly curable
	Catechol	Rapid	Highly curable

An *ortho-para* directing group in the *meta* position, such as a methyl group, enhances the reactivity of the phenol. As examples, *meta*-cresol with a methyl group in the *meta* position, is more reactive than phenol and, further, 1,3,5-xylenol with two methyl groups in *meta* positions, is several times as fast as *meta*-cresol. In resorcinol, which has two hydroxyl groups in meta position to each other, the reactivity is enhanced over both phenol and *meta*-cresol.

The speed of reaction is not always the determining factor in selecting a phenol for the production of a specific resin. Thus, *para*-substituted phenols, although slower reacting than the *meta*-substituted type, are chosen for the production of resins for use in surface coatings in preference to the others because they make resins of better oil solubility and better color stability.

Another important factor in the selection of a phenol for resin production is the size and structure of the substituent groups on the benzene ring. As one comparative example, 3,5-dimethylphenol reacts fast with formaldehyde and forms grindably-hard thermosetting resins, but the 3,5-diisopropylphenol, with its branched side chains, forms only permanently fusible resin, not hardened by heating with paraformaldehyde or hexamethylenetetramine. Long side chains on a phenol, when not branched to cause steric hindrance, generally impart solubility and plasticity to the resins made from them. Octyl, nonyl, and decyl phenols are of interest for that reason, and the unsaturated side chains of cardanol give it its desirable properties.

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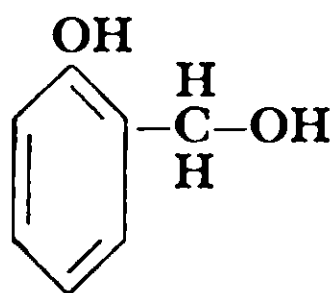
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3. RESIN PRODUCTION

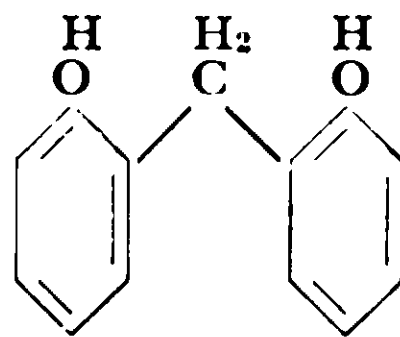
PHENOL-ALDEHYDE RESINS

Intermediate Condensation Products

Monohydric phenols show very little reactivity toward formaldehyde in the absence of catalysts. Polyhydric phenols may react under certain conditions. In the presence of either alkaline or acidic catalysts, phenols that are not structurally hindered will generally react with formaldehyde. Condensation between the two starts with the formation of a phenol alcohol type of compound. This initial product may then react with more phenol to form a diphenylolmethane type of compound.



phenol alcohol



diphenylolmethane

Both types of compounds are present in condensation products made under various conditions. The catalyst that

is used is the main factor in determining which of the two predominates. With alkaline catalysts it is the phenol alcohol type, and with acidic catalysts it is the diphenylol-methane type. As the condensation reaction proceeds, the resin molecules become increasingly complex. They may grow in a linear fashion into long chains, or they may develop much cross-linking, depending upon such factors as the nature of the catalyst used, the temperature, and whether modifying agents have been added.

The properties of unmodified phenolic resins depend mainly upon the nature and amount of catalyst used, the structure of the phenol selected, and the nature of the aldehyde and its molecular proportion in relation to the phenol. Secondary factors, such as temperature of reaction and order of addition of reactants, have a less marked influence. The properties of the resin may be modified by the addition of various materials before, during, or after the condensation. Some of these may copolymerize with the phenol, and some may act to control the phenol-aldehyde reaction in rate or direction.

The Catalysts

The catalyst may be a single chemical or a succession of different chemicals. The reaction is sometimes started with an acid catalyst and finished with an alkaline catalyst, or vice versa. A wide variety of chemical materials has been proposed for this use, and the more important ones are shown in Table 3.1. The amount of catalyst is generally specified as some percentage of the phenol charged. With acid catalysts, the amount is generally less than 1%, but in special cases it may run up to 3%. With alkaline catalysts, the average is a little higher, and the range is approximately 2 to 6%.

TABLE 3.1. CONDENSATION CATALYSTS

Type of Acid	Notes
Formic	The acidity of commercial formalin some- times suffices at elevated temperatures
Halogenated organic	Natural resin acid or ester also present ¹
Hydrochloric	In some cases, gives better results than sulfuric or phosphoric acids
Oxalic	Light-colored resins. Catalyst may be driven out under vacuum at end of the reaction
Phosphoric	Light-colored resins
Sulfamic	Resins of short cure and good water resistance ²
Sulfuric	Popular for price, lack of volatility, and ease of handling
Toluenesulfonic	Its solubility in oils helps utilization of the raw materials for the resin
Trichloroacetic	Catalyst may be decomposed into gases by heat at the end of the reaction. Light-colored resins ³

Materials Used in Acidic Medium

Salt of divalent electro- positive metal and organic acid	Active novolak, high yield of <i>ortho</i> - methylo compounds ⁴
Oxide or hydroxide of Zn, Mg, or Al	Active novolak ⁵

Alkaline Catalysts

Sodium hydroxide	Used in many liquid resin formulations
Sodium carbonate	Used in place of caustic soda for special effects
Potassium hydroxide	Used in place of caustic soda for special effects
Potassium carbonate	Used in phenol-furfural condensations
Barium hydroxide	Frequently used in combination with others
Quaternary ammonium compounds	More expensive than caustic soda
Ammonia	Puts nitrogen in the resin molecule
Primary amines	Form N-containing compounds in the resin
Secondary amines	Form N-containing compounds in the resin

Sauer and Tusch⁶ use a different approach in that they use an ion exchange resin in a fixed-bed type of reactor.

Resoles

If the reaction is carried out under alkaline conditions using one mole or more of formaldehyde per mole of phenol, the reaction when once started is capable of continuing without further addition of material until the mass has become insoluble and infusible. These resins are therefore referred to as single-stage resins. They are also called resoles.

The nature of the condensates varies with the variety of alkali used as catalyst. For example, ammonia introduces nitrogen into the polymer molecule and also produces liquid condensates with poorer water solubility than those made with caustic soda. In the production of hard resoles, several different alkaline catalysts are frequently used in succession.

Properties. In most cases in commercial production, the reaction is carried to a predetermined point and the resin is then removed from the reactor and cooled to retard the reaction and permit preparation of the resin for the applications in which it is to be used. At this stage, the resoles may be liquids of various degrees of viscosity or they may be grindably-hard resins, according to the formulation used. Properties of the commonly used types generally lie within the ranges shown in Table 3.2.

Stability. Resoles are not stable, in that the condensation reaction tends to continue until the resin is no longer workable. That may be a matter of hours or of months, depending upon the formulation used in making the resin and the storage temperature. Figure 3.1 illustrates some relationships between temperature and gel time of resoles of the type used as adhesives. At the gel point the resin has

become too thick and stiff to be workable but has not yet reached the final stage.

TABLE 3.2. PROPERTIES OF RESOLES

Liquid Resins	
Color	Reddish-brown
Specific gravity	1.15–1.30
pH	6–10
Viscosity, centipoises	35–5000
Water tolerance	Nil to infinite
Nonvolatile, %	55–75
Cure time on 150°C. hot plate, sec.	30–720
Free phenol, %	5–20
Free formaldehyde, %	2–5
Solid Resins	
Color	Tan to reddish-brown
Flow on incline plate, mm	5–150 plus
Capillary tube melting point, °C.	55–85
Cure time 150°C. hot plate, sec.	35–360
Free phenol, %	5–15

This reaction of resoles is exothermic, and the accumulation of heat of reaction of a liquid resole stored in an insulated vessel is known to have caused the resin to set up or harden in a relatively short time. Removing set-up resin from a reactor is very tedious and expensive. On the other hand, it has been found in some instances that the performance of a liquid resole in a specific application was improved by moderate aging in storage at below-room temperatures.

Cure. At the desired time, the final cure of a resole may be brought about by raising the temperature, changing the pH, or both. Catalysts may be added, if desired, to speed the reaction. A comparison of gel time of catalyzed and

uncatalyzed resins is illustrated in Figure 3.1. Commercial grades of resoles are made to various specifications, according to the use to which they are to be put.

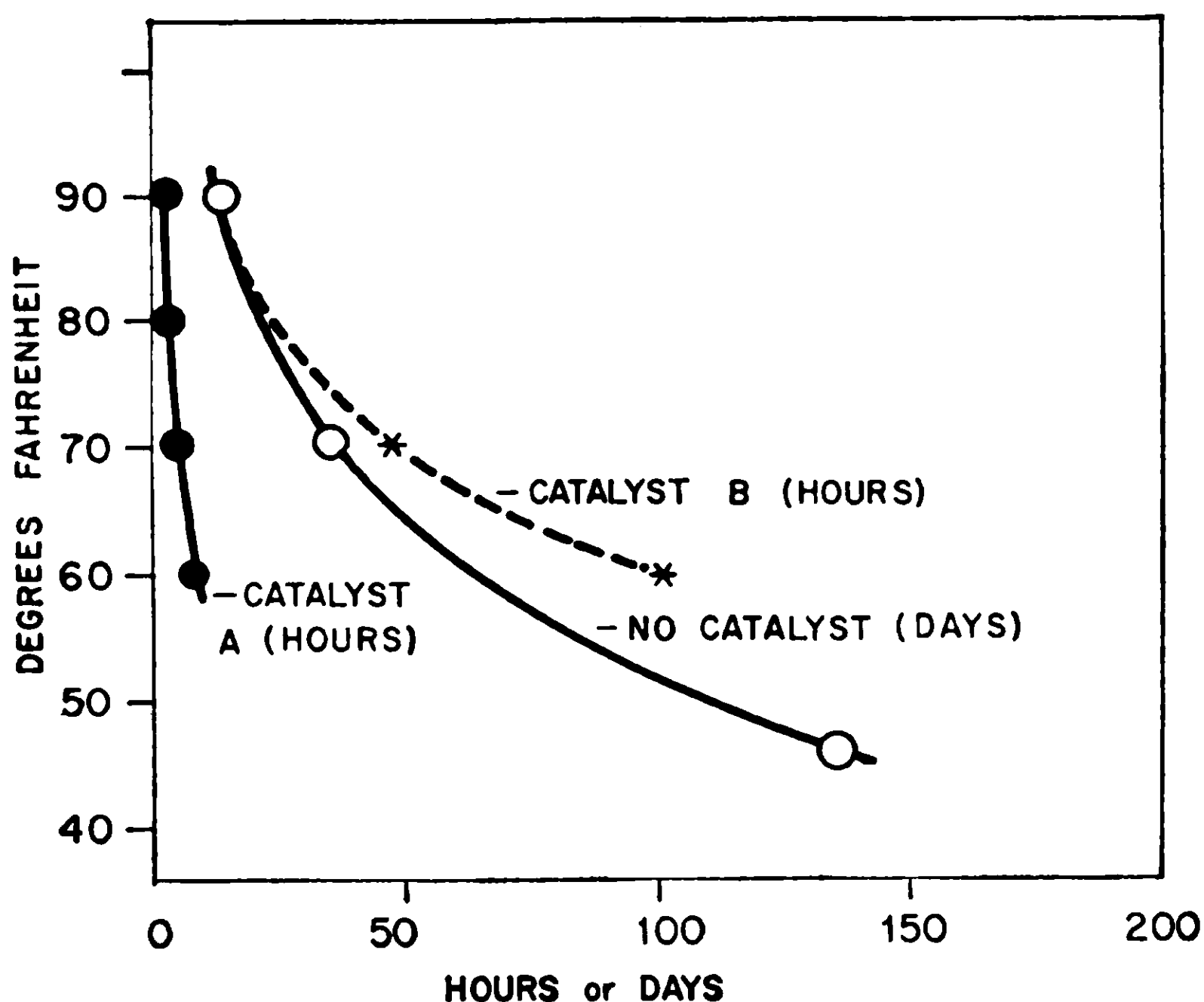


Figure 3.1. Gel time of liquid resole.

Novolaks

If 1 mole of phenol and more than 1 mole of formaldehyde are condensed in an acidic medium, the reaction goes rapidly to the formation of an insoluble and infusible product. It is more practical to start the reaction by condensing the phenol with less than 0.9 mole of formaldehyde. In this case, the reaction proceeds to the formation of a permanently fusible resin, which requires the addition of some form of formaldehyde before it will convert to the infusible, insoluble stage. Hence the use of the term two-

stage resin in referring to this type. The product of the first stage is usually called a novolak.

Acid catalysts are frequently neutralized when the condensation reaction is completed, but that leaves a salt in the resin that may not be desirable when the resin is used for some applications. As indicated in Table 3.1, oxalic acid and trichloroacetic acid offer one solution to this problem in facilitating the removal of the acid.

Novolaks are thermoplastic but are generally too brittle to be of practical use as is and serve almost entirely as intermediates for the production of thermosetting resins and of a few chemical products. They are usually prepared for further use by compounding with a hardening agent, usually hexamethylenetetramine, and sometimes also with other chemicals.

Stability. Novolaks are generally quite stable. No changes were detected after storage of samples for 4 years at room temperature and, in another case, after holding for a week at approximately 160°C. However, Hoyt and co-workers⁷ have shown that, if a novolak is made with a nonvolatile catalyst, such as sulfuric acid or phosphoric acid, and a residue of the acid remains in the product, the novolak may not be stable at temperatures of approximately 150°C. and above.

Properties. Novolak resins are somewhat hygroscopic, and should be stored in a dry place. After addition of hexamethylenetetramine, dry storage is even more important, since moisture favors reaction of the novolak with the hexamethylenetetramine and caking of the resin powder. Powder novolaks are white, pink, yellow, or tan, according to the condensation catalyst used, the metal of the reactor, the age of the resin, the grade of phenol used, and the extent of exposure to the air. Other properties are generally within the ranges shown in Table 3.3.

TABLE 3.3. PROPERTIES OF NOVOLAK COMPOUNDS

Capillary tube melting point, °C.	65–95
Cure time on 150°C. hot plate, sec.	45–110
Inclined plate flow, mm	15–60
Nitrogen analysis, %	3–7
Hexamethylenetetramine, calculated from % N	7.5–17.5
pH	6–9
Free phenol, %	8–11
Soluble in:	Alcohol Esters Ketones Alkali solutions

Uncommon Methods of Preparation. A novolak may also be prepared by condensing phenol with less than a mole equivalent of formaldehyde under alkaline conditions (*pH* 8 to 11), acidifying to a *pH* of 1 to 3 and continuing the reaction. Novolaks so prepared are claimed to have a long flow and short cure and to be suited to the production of molding powders. In the Raschig process novolaks are prepared by condensing formaldehyde with a substantial excess of phenol in the presence of ammonia. After the reaction, the excess phenol is removed by distillation.

Conversion. A novolak may react with additional formaldehyde in the presence of an alkali to form a resole. The reaction is stopped before the final stage of condensation. Blattner⁸ has shown that novolaks may be converted to resoles by heating with hexamethylenetetramine in the presence of small amounts of adipic acid.

The Aldehydes

Condensation products from phenols and aldehydes make up better than 90% of the phenolic resins produced at

present. Of the aldehydes used, only formaldehyde and furfural are commercially important. Frequently, higher aldehydes tend to self-resinify in the presence of strong acids or bases. This limits their usefulness in the manufacture of phenolic resins. Butyraldehyde and isobutyraldehyde show less tendency for side reactions, and interesting results have been obtained by using them in conjunction with formaldehyde.

Formaldehyde. This is used mainly in aqueous solution, and concentrations of up to 50% are readily obtained. As the concentration rises above 30%, it is necessary to hold the solution at increasingly elevated temperatures to prevent precipitation of a polymer that forms slowly at ordinary temperatures.

A common grade of formaldehyde for resin production is the 37% solution. This grade is generally inhibited against polymer precipitation by the addition of 7 to 15% of methanol. The methanol plays no other significant part in resin preparation. Representative requirements for this grade of formaldehyde intended for resin production are as below:

Appearance	Water-white liquid
Formaldehyde content	$37 \pm 0.2\%$
Methanol content	As required
Acidity, as formic acid	0.03% max.
pH	2.8–4.0
Iron	Trace amounts only
Copper	Trace amounts only

If an uninhibited grade can be handled in bulk and kept warm to prevent precipitation, its use offers potential savings over the inhibited grades. Where it is possible to use 44% or 50% solutions in resin manufacture, savings in operating costs result from the increase in permissible batch size and reduction in distillation requirements per lb of resin.

Paraformaldehyde. This is a solid polymeric hydrate of formaldehyde. A grade of 91% purity is claimed to give better results in the manufacture of phenolic resins than grades of higher or lower assay. Specifications are illustrated by the following:

Appearance	White flakes
Formaldehyde content	91% minimum
Ash	0.01% maximum
Melting point	100–125°C.
Iron	2 parts per million, max.

In use, depolymerization must first take place with liberation of formaldehyde, before reaction with the phenol may occur. Paraformaldehyde is produced in several degrees of activity.

Its use keeps the amount of water charged to the reactor to a minimum and the permissible batch size to a maximum.

Furfural. Furfural forms condensation products with phenols under acidic or alkaline conditions and can produce either liquid or solid products. Much has been written about phenol-furfural resins, but their production rate has never been very high and in 1956 less than a million lb was produced. Furfural-phenol condensates differ considerably in their characteristics from similar type formaldehyde-phenol condensates. Furfural reacts more slowly than formaldehyde and except for liquid, alkaline-catalyzed resin needs high temperature and anhydrous conditions for resin production.

Furfural resins have very dark colors, which has kept them out of many applications. They have found their best outlet in molding compounds, where they are generally used in admixture with phenol-formaldehyde resins. Phenol-furfural resins have a flat plasticity curve and under heat do not go through the rubbery stage characteristic of phenol-formaldehyde resins. These features make them particularly suited to the molding of parts requiring long flow.

Hexamethylenetetramine. This is a common agent for the curing of novolaks but is used in the condensation of phenol and aldehyde to only a small extent and then principally in single-stage resins. With phenols it forms molecular compounds with 1, 2, and 3 moles of hexamethylenetetramine per mole of the phenol.

Other Aldehydes. Acrolein was used in the preparation of some of the earliest phenolic resins, but price and a lack of adequate knowledge of methods of handling retarded its use. Increased availability has generated greater interest, and it is possible that it may play a more important role in the future of phenolic resins. Recently, polyphenols have been prepared from acrolein and a phenol. The polyphenols have then been reacted with formaldehyde to form resins. Numerous other aldehydes, including benzaldehyde, chloral, oxo-aldehydes, and olefinic aldehydes have been studied in the laboratory, but they are not now important in phenolic resin production.

Prereaction

It has been proposed to react an aldehyde with other materials before it is condensed with a phenol. Tetrahydronaphthalene, melamine, or urea-melamine, furfuramide, xylene-formaldehyde condensation product, and acetone are some of the materials disclosed in recent patents. They are not commercially important.

Processing

Methods used in condensing the phenol and aldehyde also vary according to the properties required in the finished resin. Mixtures of the phenol, the aldehyde, and the catalyst generally react too slowly at room temperatures for practical purposes and are brought up to about 60°C. to start

the reaction. A rapid decrease in free formaldehyde follows, with a moderate increase in viscosity of the mixture. When acid catalysts are used, the viscosity increase is accompanied by a decrease in solubility in water. The system forms two phases before the condensation reaction is complete. Efficient agitation is essential to maintain close contact of the two phases. The viscosity of the condensate levels off as the formaldehyde consumption reaches about 95%.

When alkaline catalysts are used, there may be a separation into two layers or not, depending upon the formulation. There is no leveling-off of viscosity in this case but a gradual increase which may build up suddenly until the mass gels. The problem in commercial production is to carry the reaction as far as possible and still get the resin out of the kettle and cooled without gelling.

In some instances, it is desired to have a product with a low degree of condensation, which also means a low viscosity. This is particularly of interest if the resin is to be used for impregnation. In other instances, as where quick-setting resins are needed for use in molding compounds, it may be better to run to a high degree of condensation, perhaps almost to the point of gelation.

The condensation reaction may be carried out batchwise or as a continuous process. The more common method is to charge the phenol and catalyst to the reactor and then add the required amount of formaldehyde solution. The formaldehyde may be added all at the start, in portions, or as a small continuous stream. In each case, the temperature of the reacting mass is maintained at a predetermined level. After all of the aldehyde has been added, the reactor charge is frequently refluxed for an additional period to give a higher degree of condensation. The end point of the condensation is determined by periodic tests of viscosity or melting point of the resin.

Water and unreacted volatile materials are then removed

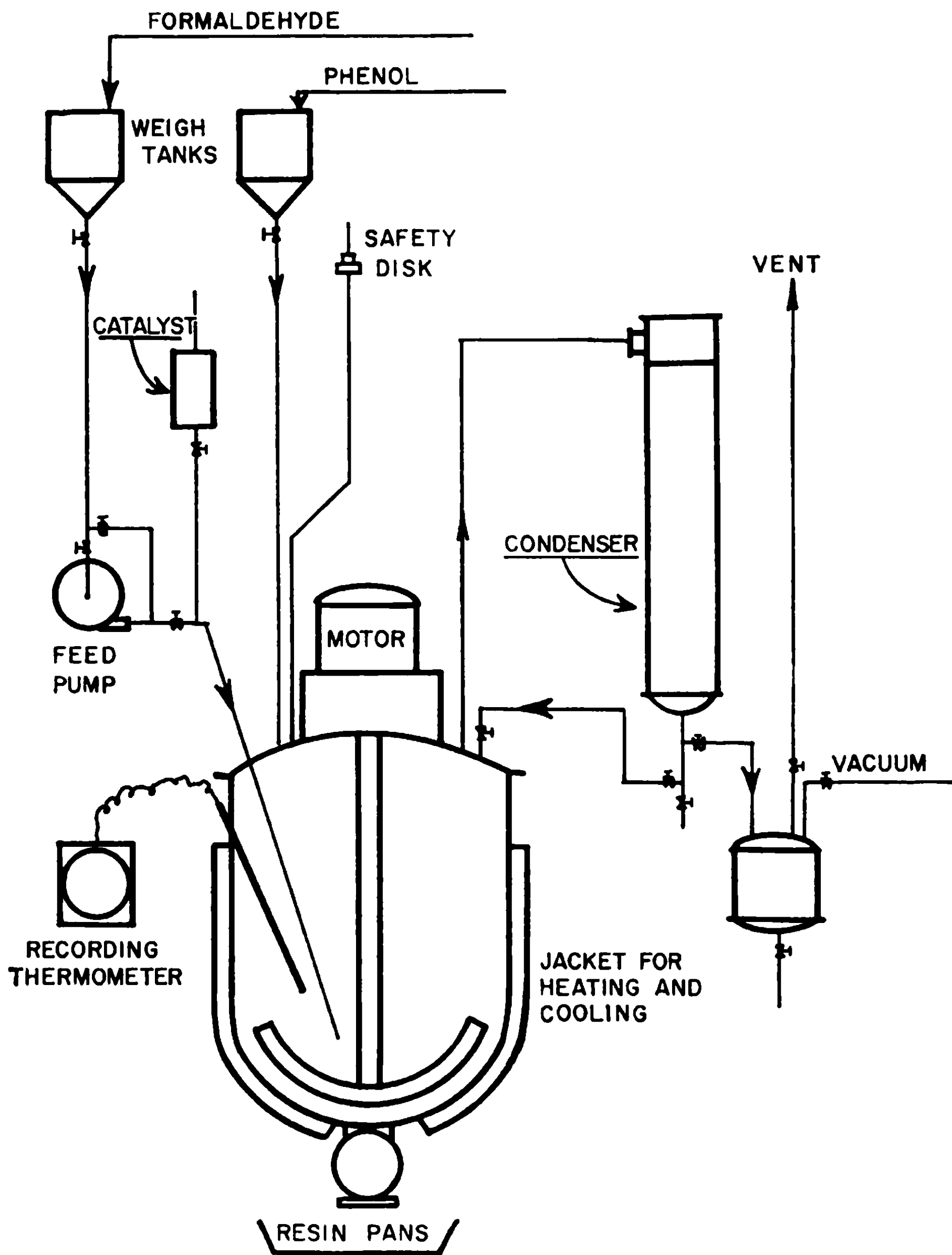


Figure 3.2. Resin kettle.

by distillation. This is generally done under vacuum to keep to a minimum the temperature to which the resin is subjected. The finished resin is run out into pans to cool or, when a grindably-hard type of resin, it may be run out onto a concrete floor. The total time to this point will vary

widely with the formulation of the resin, the type of reactor, the size of the batch, and other factors. It is usually in the range of 4 to 12 hours. After cooling, hard resins are ground and mixed with other materials, if required, in preparation for application of the resin or for further processing, as in the production of molding compounds.

Equipment. Figure 3.2 shows diagrammatically a typical arrangement of apparatus for condensing the phenol and aldehyde. The three parts of the reactor that are of particular importance are (*a*) equipment for vigorous and thorough stirring; (*b*) efficient means for heating and cooling the charge; and (*c*) a reflux condenser with adequate capacity. The condensation reaction is strongly exothermic, and refluxing is often used as a means of taking out heat during the early stages. The reactors or kettles are generally of 1000 to 3000 gallons capacity. Much resin is made in steel equipment, but lighter colors are obtained if stainless steel is used. Some types of liquid resins have shown better stability when made in stainless steel.

Other Methods. In a method that has found considerable favor, the reactants and catalyst are charged to a pressure-type reactor. The reactor is then closed and enough heat applied to start the reaction. The reaction proceeds essentially uncontrolled and is completed in a matter of minutes. This process is claimed to produce resins with superior properties for some specific applications. It is better suited to acid-catalyzed condensations, *i.e.*, the production of novolaks, than to alkaline condensations.

Continuous methods have come into use in recent years. They are suited primarily to the production of large quantities of a given grade of resin or slight variations thereof and require careful control to maintain quality. Coleman *et al.*⁹ pass phenol, formaldehyde, and catalyst through a series of coils and separators and withdraw a substantially

anhydrous resin. Houlton¹⁰ passes the reactants through an area of intense agitation and rapid heating, then through a soaking area of constant temperature to complete the reaction, and finally through a vacuum-flash still to remove volatile constituents. Bloem and Stel¹¹ use a series of vessels, through which the materials pass in cascade fashion. Several modifications have been proposed.

The three types of continuous reactors may be operated with either acid or alkaline catalysts. Time of passage of the material through the system varies approximately from 10 minutes to an hour according to formulation and equipment.

MODIFICATIONS OF PHENOL-ALDEHYDE RESINS

In 1956, 59 million lb of modified phenolic resins were produced in the United States. That was over 10% of the total phenolic resin production and does not include such resins as phenol-modified resorcinol resins. Modification of phenolic resins generally has for its purpose one or more of the following objectives:

1. Improved resin characteristics, particularly solubility, color and color stability, electrical properties, and rate of cure
2. Greater flexibility of the cured resin
3. Stronger bonding and/or adhesion to specific materials
4. Specific application performance, *e.g.*, ion exchange
5. Reduced cost

The more important methods used to modify the resin are—(*a*) adding, before condensation of phenol and formaldehyde, a substance that will cocondense with them; (*b*) reacting an intermediate phenol-formaldehyde condensate with another reactive material; (*c*) blending an interme-

diate phenol-formaldehyde condensate with a second resinous material; or (*d*) adding a chemical which will improve the properties of the phenolic resin when cured.

Rosin-modified types made up about 52% of the modified phenolics produced in 1956, and they averaged slightly lower in unit value than unmodified phenol-formaldehyde resins. Cooking of phenol-formaldehyde condensates with rosin is a well-known method of preparing resins for use in surface coatings. Preferably the condensate used is one made from alkyl phenols by alkaline condensation. Phenolic resins for surface coatings are also modified by high-temperature treatment with drying oils.

Aniline-Modified

These types made up about 7% of the modified phenolics produced in 1956. The phenolic is modified by treatment of an intermediate phenol-formaldehyde condensate with aniline or aniline derivatives, by cocondensation, or by blending a phenol-formaldehyde condensate with an aniline-formaldehyde condensate. Aniline-modified phenolics have particularly good electrical characteristics, and they average about 20% higher in unit value than unmodified phenol-formaldehyde resins.

Copolymers

Over the past years, a great many modifications have been proposed. Some of the interesting materials used to form copolymers are:

Amines

For resins having ion exchange properties

Chlorinated phenols

Flame-resistant resins, linear polymers, less viscous and faster curing intermediates

Nitromethane	High bond strength thermosets
Organosilicon compounds	Heat-stable resins
Sucrose	Lower cost resins
Urea or melamine	Good molding and laminating properties

Treatment of Intermediates

Some of the materials used to treat intermediate phenol-formaldehyde condensates are:

Epichlorohydrin	Improved color and alkali resistance
Ether resin	Flexibility in the hardened resin
Ethylene oxide polymers	Shaped articles which may be worked
Hydrogen peroxide	Faster curing resin
Ketones	Cold hardening resins for adhesives, etc.
Methylolaniline HCl	Increased melting point
Polyvalent salts of hexanoic acid	Hardening properties improved
Stannous chloride	Metal-containing polymer
Terpene-phenol product	High-melting resins, good film strength

Resin Alloys

There are certain similarities between the blending of resins and the blending of metals. To be sure, there are also great differences, involving such items as the curing reaction of the resins on the one hand and the crystallization of metals on the other. The objectives of the blending are essentially the same for metal alloys as for resin alloys, and one or more of the following are usually involved:

- Cost reduction with minimum loss of properties
- Greater or lesser hardness

Improved mechanical strength
Higher melting point
Improved chemical resistance
Improved electrical characteristics

A great deal has been done on the development and application of phase diagrams for metal alloys, and the work has been very profitable in the design of alloys for particular purposes and in utilizing materials to best advantage. Resin alloys have developed mostly on a cut-and-try basis. The good results obtained in many cases, and the growing evidence of the effect of minor additions to phenol-aldehyde condensates, lead to the thought that a more systematic approach to resin alloys on a phase-diagram basis might be highly profitable.

Blends

Blends of various materials with phenolic resins are too numerous for a full discussion here. Some of the more common blends are shown below, others are discussed in the chapters on applications.

Material	Use
Epoxy resins	Binders, molding compounds
Furfuryl alcohol resins	Solvent- and alkali-resistant resins
Ketone-aldehyde condensates	Plywood adhesives
Melamine and urea resins	Adhesives
Natural and synthetic rubber	Adhesives, molding compounds
Polyvinyl acetal resins	Binders and specialty adhesives
Polyvinyl chloride	Electrical insulation

The combination of synthetic rubbers and phenolic resins is particularly interesting. Small proportions of certain elastomers added to a phenolic resin aid in making a molding compound from which molded parts of improved shock resistance may be made. Small proportions of specific

types of phenolic resins give hardness and improved properties to rubber compounds, such as are used in shoe soles, for example. The vulcanization of butyl rubber with a resole phenol resin or with dimethylophenol is somewhat beyond the region of simple blends.

CURING OR HARDENING

The curing or hardening of a phenol-formaldehyde condensate involves a very complicated series of chemical reactions, which is far from thoroughly understood. The end result is the formation of a network by the cross-linking of the many linear and branched polymer chains formed during the previous reactions. The cross-linking occurs best when there are methylol groups present in the polymer molecules. In order to cure the polymer to the insoluble and infusible stage, it is also essential that there be at least one mole and preferably about $1\frac{1}{2}$ mole of formaldehyde or other suitable aldehyde per mole of phenol.

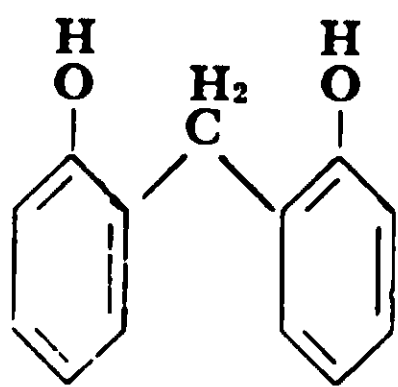
Resoles

Resoles are normally made with sufficient aldehyde to permit curing, and in order to complete the cure it is only necessary to raise the temperature of the resole to speed the reaction. For a faster cure or to cure at lower temperature, an acidic agent is added to bring the *pH* of the system to a relatively low level. Phenolsulfonic acid, *p*-toluenesulfonic acid, hydrochloric acid, and phosphoric acid are the ones frequently used. Oxidation can also play a part here, and the use of inorganic oxidizing agents and specifically of chromates and dichromates has been disclosed.

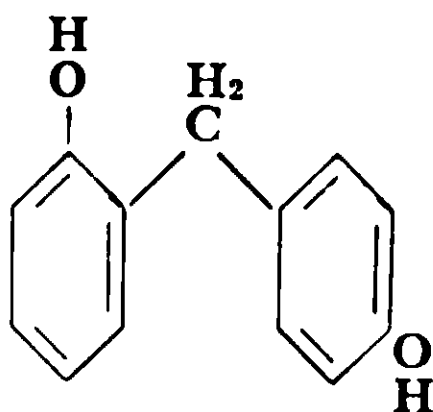
Novolaks

By themselves novolaks do not cure. They are intentionally prepared with a deficiency of formaldehyde, and they also lack methylol groups in their structure. In order to cure them, some form of formaldehyde or formaldehyde donor must be added, to bring the ratio of formaldehyde to phenol to the proper level for curing. In commercial practice, hexamethylenetetramine ("hexa") is commonly used and is blended in finely divided form with the pulverized resin. Under the influence of heat, the hexa breaks down into formaldehyde and ammonia, and the formaldehyde reacts with the novolak under alkaline conditions. Presumably, methylol groups are produced and through them the cross-linking essential to curing takes place.

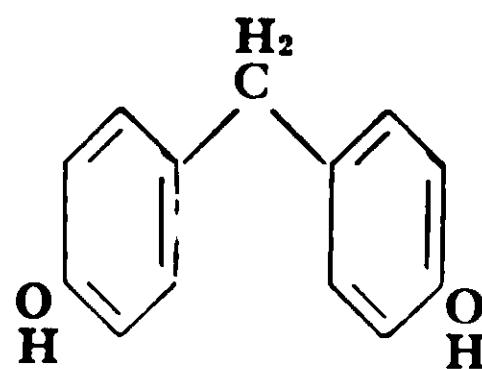
Intermediate Products. Dihydroxydiphenylmethane isomers are predominant in the initial stages of the acidic condensation of phenol and formaldehyde. There are six isomers, but only three are of primary interest in phenol-formaldehyde condensations. They are 2,2', the 2,4', and the 4,4' isomers. Bender has shown that there is a substantial difference in the reaction rate of these three isomers as indicated by the gel time observed on heating the dihydroxydiphenylmethane isomer with 15% of hexa on a hot plate at 160°C.^{12, 13}



isomer—2, 2' (ortho-ortho)
gel time—60 sec.



2, 4' (ortho-para)
240 sec.



4, 4' (para-para)
180 sec.

The same authors have also shown that, in the alternate addition of phenol and methylene groups to form the novolak chain, the addition of methylene groups to the 3 and 3' positions produces the fastest reacting resins. Addition of the methylene groups at the 5 and 5' positions gives resins that are substantially slower reacting. By proper selection of these structural factors, they were able to produce resins which hardened on the 160°C.-hot plate in 5 to 10 seconds as compared to 20 to 85 seconds for the usual commercial types of resins. Applying these findings to the production of resins for use in molding powders, reductions of 15 to 25% in molding times are indicated, which is highly important commercially.

Hexamethylenetetramine (Hexa). The amount of hexa used is commonly about 10% of the novolak. Increasing the amounts up to 15% has little additional effect. Activity of hexa is improved by the addition of a controlled amount of lime to the novolak mixture. Excessive amounts tend to cause brittleness in the cured resin.

The novolak and hexa are usually ground together to get intimate mixing. Grinding as intensively as possible without generating undue heat in the mill favors the curing properties of the resin. The addition of a small amount of water to the mix also helps. This may be due to the formation of a complex between the novolak and the hexa, similar to the phenol-hexa complex referred to previously.

A finely ground novolak suspended in an aqueous solution of hexa will absorb approximately the amount of hexa necessary to cure a novolak.

Other Curing Agents. Various other compounds have been suggested as curing agents for novolak resins. Anhydroformaldehyde-aniline, ethylenediamine-formaldehyde products, and methylol derivatives of urea or melamine are among them. They are of much less commercial importance

than hexa. Paraformaldehyde, which serves satisfactorily in the initial condensation with a phenol, is a poor curing agent for novolaks made from monohydric phenols. Novolaks made from resorcinol or resorcinol-phenol behave in an opposite manner. There, paraformaldehyde is used regularly as a hardening agent, while hexa is a poor hardening agent.

Monomethylol dimethyl hydantoin has recently been offered as a formaldehyde donor. It is considerably less reactive with resorcinol resins at room temperature than paraformaldehyde, which can be an advantage under certain conditions, as when an adhesive with long pot life is needed.

Precure

Several devices have been used to bring phenol-formaldehyde condensation products as closely as possible to the gelling and hardening stage while still remaining workable. This minimizes the time required to complete the cure. One method is to heat the resole or the novolak-hexa mixture in pans at moderate temperatures below the melting point of the resin.

Epstein¹⁴ has refined this as applied to the curing of phenolic resin adhesives for metal to metal bonding. He has shown that, using phenolic resins made with alkaline catalyst, a threefold increase in tensile-shear strength of aluminum specimens tested at 500°F. is obtained if the cure is carried out in two steps instead of the usual single step. Coated parts were oven-dried at 180°F. for one hour to get a soft set of the resin, then assembled, and cured at 275°F. for 60 to 90 minutes under a pressure of 50 to 100 psi.

Coleman and Sutherland¹⁵ follow the formation of a

novolak with a treatment with 0.5 to 3% of hexamethylenetetramine in aqueous solution, to produce a resin with low flow and short cure. With some novolaks, addition of that amount of hexa has gelled the resin.

OTHER TYPES OF RESINS

Many combinations of phenols with materials other than saturated aldehydes have been disclosed. They are recommended for practically all the general classes of use of phenolic resins. Many of them never progressed beyond the laboratory.

Notes on some selected combinations appear in the following paragraphs. Some are in minor commercial production, some are interesting newcomers that seem to have possibilities, and some are examples of attempts to use lowest-cost raw materials. In attempting to reduce resin costs by using low-cost reactants with phenol, it frequently happens that the saving is used up to a large extent by increased processing cost.

Acetylene-Phenol

Hard transparent resins can be produced from phenol and acetylene. The major commercial example is "Koresin," a rubber tackifier made from *tert*-butylphenol and of European development. These resins are dark-colored, quite hard, and rather expensive.

Acrolein-Phenol

Condensation products of phenol and acrolein were among the earliest phenolic resins. The product of the methods used then showed no practical advantages and is

not manufactured. Several studies of the reaction have been made since then.

Recently, Farnham¹⁶ has disclosed the production of triphenylol and other polyphenylols by the reaction of a monohydric phenol with acrolein or other unsaturated aldehyde. These products are of relatively low molecular weight and can be reacted with epichlorohydrin to give epoxy resins or with formaldehyde or other saturated aldehyde to give phenolic resins.¹⁷

Facilities for production of acrolein have been expanded, and there is better understanding of methods of handling and of its applications in chemical reactions. These could give an impetus to its use in resins.

Cellulose-Phenol

Novotny and Romieux¹⁸ found that by heating phenol and wood flour liquid, semisolid, and solid resins could be obtained. The solid resin was hard, brownish-black, lustrous, and high-melting, and could be hardened by adding small proportions of furfural and heating.

Cyclopentadiene-Phenol

At temperatures above 200°C. and using a large amount of catalyst, hard dark resins are produced. They are resistant to acids and to alkalies.¹⁹

Ketone-Phenol

Phenol condenses with acetone or methyl ethyl ketone in the presence of a catalyst to a shellac-like solid. Hexamethylenetetramine and other agents convert the condensate under heat and pressure to a hard, infusible, and resistive material. The resin is said to be satisfactory as a

binder in the production of laminates or other forms of electrical insulation. It is not competitive pricewise with phenol-formaldehyde.

Vogelsang^{20, 21, 22} has disclosed the preparation of versatile resinous products by the interaction of ketone-aldehyde condensates and phenol-aldehyde condensates. The products are useful for impregnating paper and textiles, as adhesives and bonding agents, as ion exchange resins, and as components of molding compounds.

Lignin-Phenol

The availability and low price of lignin have led to much experimental work on its utilization. United States patent 2,221,282 gives one example of its use in resins. Phenol and lignin are heated in the presence of sulfuric acid, and lustrous, brittle, black resin is recovered. The resin is converted to a hard, insoluble and infusible form by heating, with or without a hardening agent. It is suggested for use in varnishes, as an impregnant, and as the binder in molding compounds.

Lignite-Phenol

In Europe, powdered lignite was heated with cresol in a volatile solvent until swelling of the lignite occurred. After removal of the solvent, the mass was pressed at about 150°C. and 4000 psi. It was marketed under the name "Kolinit."

Polyhydric Phosphorus Compound-Phenols

Various phenolic compounds can be condensed with a polyhydric phosphorus compound, such as tetrakis-

(hydroxymethyl)-phosphonium salts, tris-(hydroxymethyl)-phosphine oxide, or a phosphorus-linked methylol-containing derivative.²³ The resins are resistant to burning and are valuable in varnishes, surface coatings, and molded articles, where high heat resistance is desired.

Polyisocyanate-Phenols

Phenols with two or more phenolic nuclei react with polyisocyanates to give resins said to be useful in paints, lacquers, and adhesives.²⁴

Silicic Acid Ester-Phenol

German patent 1,009,813 discloses the production of high-molecular weight polymers from a phenol and a silicic acid ester. They are suggested as cross-linking agents for linear polymers.

Starch-Phenol

A dark product was obtained by acid-catalyzed condensation. It could be hardened by long heating at about 125°C. Hardening was hastened by hexamethylenetetramine. The cured product was hard, infusible, and insoluble in most solvents. Incorporation in coatings and impregnation of fibrous material were suggested as outlets.

Styrene-Phenol

Styrene and phenol form viscous-liquid to solid products when heated in the presence of a catalyst. Fuller's earth, phosphoric acid, and borofluoroacetic acid are among the catalysts used. The products are not strongly resinous, and

they are used as plasticizers and in combination with drying oils in surface coatings.

Sulfur-Phenol

Condensates are produced by heating with or without catalysts. Uses suggested for the product are molding compositions, coatings, mordant for dyes, fungicide, and rubber preservative.

Terpene-Phenol

Terpineol or dipentene and phenol can be condensed in acidic solution to form very pale, thermoplastic condensates. These are used in rubber and surface coatings and as a wax additive.²⁵ Cyclic terpenes and phenols are condensed in the presence of polyphosphoric acid to yield terpene diphenols, claimed to be useful in coating compositions.²⁶ Been and Grover²⁷ heat a phenol-aldehyde resin with a terpene-phenol resin to form new resins, said to be useful in coatings, adhesives, varnishes, and heat-set inks. The resins are dark-colored, brittle, and may have melting points in excess of 150°C. Esterified terpene-phenol condensates have been suggested as components of self-polishing wax.

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4. MOLDING COMPOUNDS

During the past five years an annual average of 207 million lb of phenolic molding compounds was produced and used in the production of parts ranging in weight from a few grams to several tons. Recently, the average price has been about \$0.25 per lb. Special types sell for several times that amount.

Four forms of phenolic materials are used for molding, and they are:

1. Granular powders which are putty-like when hot and uncured
2. Random-laid fibers coated with resin
3. Chopped fabric saturated with resin
4. Resin and fillers plasticized with solvents

All four forms are thermosetting. There is an area in which molded materials of this group overlap, in make-up and production, the laminated products considered in Chapter 6.

Phenolic materials have been limited somewhat by their color, time required for curing, and heat-distortion tem-

perature. Substantial improvements that have been made in the last few years on all three properties have lessened their limitations. Combinations of melamine and phenolic resins are now molded in pastel shades. The cure time of phenolic resins has been reduced in some instances as much as 70%. This permits phenolics to be molded at speeds approaching that of injection molding of thermoplastics. New resins have been developed that have stood long exposures to temperatures of 500°F. or higher, and short exposures to much higher temperatures.

Classes of Compounds

There are two groups of phenolic molding compounds. The "Low Reinforcement Group" or the "Powder Molding Compounds," includes types usually referred to as general-purpose, electrical, and chemical resistant, together with some varieties of heat-resistant compounds and special property compounds.

The "High Reinforcement Group" includes compounds containing a high proportion of inorganic or organic fibrous material other than wood flour. Impact types and most of the heat-resistant types belong in this group, as do resin-glass fiber and resin-wood chip compounds. Production and molding methods differ in several respects from those used with the previous group.

Standards for Molding Compounds

The American Society for Testing Materials has set up standards for molding compounds as "ASTM Specification D 700, Specifications for Phenolic Molding Compounds." Type classifications and physical properties are quoted in Tables 4.1 and 4.2. Molded parts may give different values

TABLE 4.1. MOLDING COMPOUND TYPES*

-
- Type 2.* General-purpose wood flour-filled material suitable for electrical applications. When requiring a single-stage resin add the letters SS, that is, Type 2 SS (Note 1).
- Type 3.* General-purpose material with a cellulose filler which may be wood flour or cotton flock. It is somewhat higher in impact strength than Type 2 and suitable for both mechanical and electrical applications (Note 2).
- Type 4.* Moderate impact strength material with chopped cotton fabrics or other suitable forms of cellulose filler to give the required strength for this type (Notes 2 and 3).
- Type 5.* Medium impact strength material with chopped cotton fabrics or other suitable forms of cellulose filler to give the required strength for this type (Notes 2 and 3).
- Type 6.* High impact strength material with chopped cotton fabric, chopped cord, or other suitable forms of cellulose filler to obtain the required strength for this type (Note 3).
- Type 7.* An electrical high-frequency low-loss material with a mineral filler (Note 4).
- Type 8.* A superior electrical high-frequency low-loss material with a mineral filler (Note 4).
- Type 9.* A heat-resistant, mineral-filled material with added mechanical strength.
- Type 10.* Heat-resistant mineral-filled material.
- Type 11.* A general-purpose wood flour-filled material suitable for mechanical applications. When a single-stage resin is required add the letters SS, that is, Type 11 SS (Note 5).
- Type 12.* A general-purpose shock-resistant material with paper, flock, or pulp filler.
- Type 13.* A low-gravity heat-resistant material containing mineral and other fillers.
- Type 14.* General-purpose wood flour-filled rubber-modified phenol-plastic.
- Type 15.* General-purpose rubber-modified phenolplastic with a cellulose filler which may be wood flour or cotton flock.

TABLE 4.1. MOLDING COMPOUND TYPES (Contd.)

Type 16. Moderate impact strength rubber-modified phenolplastic with chopped cotton fabrics or other suitable forms of cellulose filler to give the required strength for this type.

Type 17. Medium impact strength rubber-modified phenolplastic with chopped cotton fabrics or other suitable forms of cellulose filler to give the required strength for this type.

Type 18. Heat-resistant mineral-filled rubber-modified phenolplastic.

NOTE 1. A single-stage resin meeting the requirements of Type 2 may produce less tarnish and, therefore, be superior in some special electrical applications.

NOTE 2. To secure the optimum electrical qualities inherent in these materials, they must be dried to remove surplus moisture prior to molding. Powder should be spread in shallow nonmetallic pans, preferably in a rotating oven. Preformed material should be supported in such a way as to heat evenly. Material for test specimens must be dried immediately prior to molding and molded while still warm. Warming for 30 min at 85 C. (185 F.) usually suffices, or shorter times at higher temperatures may be used, although more care may be required to prevent precuring the material.

NOTE 3. In all cases there will be some sacrifice in appearance and moldability.

NOTE 4. The powder must be dried before molding as described in Note 2.

NOTE 5. A single-stage resin meeting the requirements of Type 11 usually imparts less odor and taste.

* From A.S.T.M. Specification D-700.

at times due to the effects of design of the part and the method of molding.

The types shown in these classifications are frequently subdivided in two ways. Usually, a given type of molding compound is produced in degrees of softness at molding temperatures ranging from very stiff to very soft. They are designated by some system of arbitrary flow numbers,

TABLE 4.2. DETAIL REQUIREMENTS FOR MOLDED TEST SPECIMENS^a

	Type 2 ^a	Type 3	Type 4	Type 5	Type 6	Type 7	Type 8	Type 9	Type 10
Water absorption, max, weight gain, per cent	0.80	0.80	1.50	1.75	1.75	0.10	0.07	0.20	0.20
Specific gravity, 23/23 C. (73.4/73.4 F.) max ^b	1.45	1.45	1.45	1.45	1.45	2.00	2.00	2.00	2.00
Flexural strength, min, psi	9 000	9 000	9 000	9 000	9 000	8 000	8 000	9 000	7 000
Impact strength (Isod), min, ft-lb per in. of notch	0.24	0.34	0.80	1.75	4.00	0.30	0.30	0.64	0.25
Tensile strength (1/8-in. specimen), min, psi	6 500	6 500	5 500	6 000	6 000	4 500	4 000	4 500	4 000
Compressive strength, min, psi	22 000	22 000	20 000	18 000	15 000	15 000	15 000	15 000	15 000
Modulus in flexure, max, psi	—	—	—	—	—	—	—	—	—
Mold shrinkage, in. per in. ^c :									
Min	0.003	0.003	0.002	0.002	0.003	0.001	0.001	0.001	0.002
Max	0.008	0.008	0.007	0.006	0.006	0.005	0.005	0.005	0.006
Insulation resistance, min, megohms	100	100	10	10	—	300	300	—	300
Dielectric strength, min v per mil:									
Short-time test	275	240	200	200	—	300	325	—	300
Step-by-step test	225	200	150	150	—	250	300	—	200
Dielectric constant, max	—	—	—	—	—	6.5	6.0	—	—
	—	—	—	—	—	5.2	5.0	—	—
Dissipation factor, max	—	—	—	—	—	0.07	0.025	—	—
	—	—	—	—	—	0.02	0.010	—	—
Loss factor, max	—	—	—	—	—	0.46	0.150	—	—
	—	—	—	—	—	0.10	0.05	—	—

TABLE 4.2. DETAIL REQUIREMENTS FOR MOLDED TEST SPECIMENS* (Contd.)

	Type 11 ^a	Type 12	Type 13	Type 14	Type 15	Type 16	Type 17	Type 18
Water absorption, max, weight gain, per cent	0.80	1.20	0.5	1.5	1.5	1.5	1.5	0.3
Specific gravity, 23/23 C. (73.4/73.4 F.) max ^b	1.45	1.45	1.68	1.35	1.35	1.35	1.35	1.70
Flexural strength, min, psi	9 000	9 000	7 000	7 000	7 000	7 000	7 000	8 000
Impact strength (Izod), min. ft-lb per in. of notch	0.24	0.46	0.23	0.35	0.45	0.80	2.00	0.30
Tensile strength (1/8-in. specimen), min, psi	6 500	6 500	4 000	3 500	4 000	4 000	4 000	4 000
Compressive strength, min. psi	22 000	22 000	15 000	15 000	15 000	15 000	15 000	15 000
Modulus in flexure, max, psi	—	—	—	4 × 10 ⁵	4 × 10 ⁵	5 × 10 ⁵	5 × 10 ⁵	8 × 10 ⁵
Mold shrinkage, in. per in. ^c :								
Min	0.003	0.003	0.003	0.005	0.004	0.004	0.002	0.004
Max	0.008	0.008	0.006	0.010	0.009	0.008	0.008	0.008
Insulation resistance, min, megohms	—	10	—	100	100	100	100	100
Dielectric strength, min v per mil:								
Short-time test	—	240	—	275	300	275	250	275
Step-by-step test	—	200	—	225	275	225	200	225
Dielectric constant, max	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
Dissipation factor, max	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
Loss factor, max	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—

^a Compounds of Types 2 and 11 may be furnished with either single-stage or two-stage resin. In the event single-stage resin is required, the type designation should be followed by the letters "SS." Single-stage compounds shall have a maximum free-ammonia content of 0.02%.

^b Colored compounds other than natural or black may exceed the limits specified by 10% because of heavy pigmentation.

^c The limits given for shrinkage are representative for a wide variety of materials of any given type. Shrinkage of any specific compound, as measured by the method prescribed, will generally vary much less.

^d From Specification D 700-57T, American Society for Testing Materials.

of which there are several in use by various manufacturers. The other method of subdivision is on the basis of the value of some property, such as the range of impact strength of certain types of compound, the absence of odor and taste in a general-purpose type compound for use in closures, or the quality of a compound that permits sanding and buffing to a high finish without showing specks of filler.

LOW-REINFORCEMENT GROUP

This group constitutes the larger part of phenolic molding compound production. Basically they are composed of a resin, a filler, and small amounts of auxiliary materials.

Resins

Novolaks are used for the major part of this group. Instability in storage of resoles either as resin or as molding compound limits commercial use. They are used occasionally where their properties are particularly necessary, as in the production of molded closures free from ammonia odor. Mixtures of phenolics sometimes cure faster than a single resin. A minor proportion of phenol-furfural resin blended in helps the flow and molding properties of the compound.

Resin Compound

Novolaks are first made into a dry mix or resin compound by grinding with approximately 10% of their weight of hexamethylenetetramine plus a small amount of a curing accelerator such as lime. During the grinding a partial reaction of the resin and the hexamethylenetetramine takes

place. This is aided by traces of water. The preparation of the resin compound helps to give a more consistent curing property to the molding compound.

Fillers

Wood flour is the filler most widely used in this type of molding compound. It is prepared from selected species and is frequently made from white pine or Douglas fir. The wood must be free from bark, knots, and resin spots, all of which cause blemishes in molded pieces. Grinding is done in such a manner that the fibrous structure of the wood is maintained as far as possible.

Several materials containing resinous substances have been proposed for use in conjunction with wood flour. "Silvacon," a derivative of bark, has found considerable use.

In the production of heat-resistant compounds, wood flour is usually replaced by short-fiber asbestos. When electrical properties are important, the asbestos is usually acid-washed to remove impurities affecting electrical measurements.

Charcoal, clay, graphite, ground limestone, mica, and powdered nutshells are some of the other fillers used to get particular effects in molding properties, surface finish of molded pieces, heat resistance, electrical properties, or specific gravity.

Auxiliary Materials

Zinc stearate or other metal stearate or a wax such as montan is added as a lubricant to improve the molding properties of the compound. Nigrosine dye and carbon black are used for color in black compounds and appropriate pigments in compounds of other colors.

Many materials have been proposed as additives to phenolic molding compounds to help flow, hasten cure, plasticize, or reduce cost. These have had only limited use. Improvement in rate of cure has come from modifications of the formulation and the processing of the resin rather than from additives. Anything low enough in price to reduce the cost of phenolic molding compounds appreciably usually also reduces the physical properties of the molded parts.

The most successful additive to phenolic molding compounds appears to be the butadiene-acrylonitrile type of synthetic rubber.¹ Molding compounds containing minor proportions show superior shock and fatigue resistance and mold well around inserts without subsequent cracking. These advantages are obtained at a sacrifice of tensile, flexural, and compression strengths, hardness, and cure time. In some applications these sacrifices are fully justified.

Compounding on Rolls

The resin compound, fillers, and other ingredients are blended and fed to a pair of rolls held at controlled temperature and operated at a low differential in speed. The compound is plasticized by the heat and ground by repeated passage through the narrow space between the rolls until the filler is thoroughly wetted by the resin. The heat advances the cure of the resin somewhat. The plastic mass is then cut from the rolls, sheeted out, and cooled.

Several variations of equipment and procedure are used. In some plants, the dry powders are fed continuously to the rolls and the product removed continuously. At present, automation of intermittent feed and intermittent removal of product appears to be the best answer to economical and uniform operation.

After cooling, the compound is fed to a series of crushers, grinders, and sieves where it is reduced to the desired fineness. The screened product is then blended, preferably in lots of 30,000 to 50,000 lb to insure uniformity of truck-load or carload shipments. Blending also reduces the bulk density of the compound.

Other Methods of Compounding

Extruders have been adapted to the combined mixing and extrusion of phenolic molding materials.^{2,3} They have been used in the production of impact-grade materials but have not come into common use. Operational savings are claimed for the production of phenolic molding compounds in jacketed, double-blade, trough-type kneader mixers.⁴ Similar equipment has been used for years on impact-type compounds but the production of general-purpose compounds remains to be worked out. If that is successful, captive production of molding compounds would be attractive to molders.

Where sizable pieces are molded and the cure time is 3 to 4 minutes or longer, it has been found practical to locate suitable size rolls adjacent to the press. The hot batch is then cut from the rolls and placed in the mold. This avoids all of the usual operations between the rolls and the press.

Quality Control

Three properties of a molding compound are of special importance and require checking throughout the process, from dry blend to final product. They are molded appearance, flow properties, and rate of cure.

The final blend is examined not only for these characteristics but also for particle-size distribution, mechanical strength and electrical properties as required. If the compound is to be preformed into blocks or pellets for molding, its preforming characteristics are also checked.

HIGH-REINFORCEMENT GROUP

This group merges with the low-reinforcement group on one side and with laminated products on the other. It includes both long-established asbestos- and cotton-filled compounds and new phenolic resin-and-glass fiber materials that are prominent in missile construction. Through the performance of this group, a change is being effected in the attitude of industry toward phenolic resins. Commonly they have been regarded as merely general-purpose materials economically priced. Now it is being recognized that they have among them special-purpose materials that offer desirable properties at economies beyond other materials.

These materials are distinguished from the molding compounds of the preceding section by the character of the fillers used and the methods of preparation. Impact resistance and heat resistance are substantially improved over general-purpose compounds but are still much inferior in those respects to the new compounds for missile work.

Resins

Here phenolic resins hold an essentially exclusive position. Both novolaks and resoles are used. Liquid resins or resins that may be liquefied by the addition of minor proportions of solvent are preferred.

TABLE 4.3. WOOD FLOUR VERSUS FIBERS IN MOLDING COMPOUNDS

	Wood Flour	Asbestos Fibers #1	Fibers #2*	Random	Glass Fibers Orientated
Bulk factor	2.6	4.5	12	6.1	
Preforming—Normal equipment	×				
Special devices		×			
Hand feed			×	×	×
Specific gravity	1.38	1.84	1.87	1.84	
Molding shrinkage, thousandths in./in.	6-8	2.5-3.5	1-2	0	
Impact strength, Izod, ft-lb/in. notch	0.30	0.6	0.85	12	27
Tensile strength, psi	7000	4600	4500	7000	24000
Heat resistance, not over °F.	310	450	450	600	
Dielectric strength, short time, v/mil	320	250	250	275	

* Larger proportion of long fibers than in #1.

Fibers

Physical properties of the molded parts are determined mainly by the nature of the fibers used, the length of the individual fibers, and the proportion of fibers in the compound. Some of the effects obtained in changing from the wood flour filler used in the low-reinforcement molding compounds to the fibrous fillers of this group are illustrated by the data in Table 4.3. If the preparation of the compound and the molding can be so handled that the fibers are oriented and remain so, remarkable increases in strength along the direction of orientation are obtainable. Data in the last column of Table 4.3 illustrate this.

Asbestos is the most widely used inorganic fiber. Paper, cotton flock, cotton thread or cord, and chopped cotton fabrics are the vegetable fibers used. The higher absorption of resin by cellulose fillers as compared to mineral fillers makes a difference of 5 to 10% in the resin content of the compound by weight.

Bulk Factor

The ingredients that increase the impact strength of these compounds also make necessary the use of special methods of processing. The ratio of volume of loose molding compound to the volume of the same weight of material after molding is bulk factor to the molder and is very important to him. As the amount of long-fiber material in a compound is increased, the product becomes fluffier and the bulk factor increases. This is shown by the data in Table 4.3. Special handling is required in molding since the fluffy product does not pour well and cannot be preformed in the equipment that is normally used with general-purpose molding compounds.

Compounding

Production on differential rolls is not satisfactory because the grinding action between the rolls breaks down the fibers and reduces the impact strength of molded parts. Sigma blade mixers have given good results, and in some instances pug mills have been effective. Spiral blade mixers are much less effective than the sigma blade type. Screw type extruders have been adapted to the compounding of phenolic molding compounds.^{2,3} Compounds of intermediate strength have been produced satisfactorily in such equipment. By use of suitable attachments, the product of the extruder is delivered in easily-handled pellet form.

The production of molding compounds of high and uniform quality requires a balance between wetting of the fibers by the resin, removal of volatiles without case-hardening of the resin-filled particles, advancement of cure of the resin, and avoidance of degradation of the fibers. The simplicity of equipment required for production of compounds in sigma blade mixers has led to the suggestion that molders mix their own compounds.⁴

Frequently the compound is delivered from the mixer in a form that can be used directly by the molder. In other cases it is necessary to run it through a cutter before molding.

Grades

These molding materials are produced in several ranges of impact strength. Properties of some of them are given in Tables 4.1 and 4.2. Classifications used by Government agencies such as the U.S. Navy Bureau of Ships are important in industry. Cost of compound and difficulty of molding increase with increase of impact strength. Overspecifica-

tion of impact strength for a given application is therefore avoided as far as possible. The selling price of these compounds averages about 67% higher than the average of general-purpose molding compounds. For some grades the differential may be 100%.

COMPOUNDS OF MAXIMUM HEAT- AND IMPACT-RESISTANCE

These compounds have come into special prominence with the development of high-speed airplanes, missiles, satellites, and rockets. They are specialty items at present and are competitive on performance rather than on price. Phenolic materials have a combination of high-heat resistance, rigidity, and good adhesion to reinforcements that is superior to that of any other plastic. This is of particular interest in the applications mentioned above. Lack of adequate information on performance in the hands of potential users is said to be one of the main obstacles to increased use.

Resins

The common types of phenolic resins do not have the very high heat resistance plus impact resistance that is demanded for modern missile and airplane use. Resoles have an advantage over novolaks in that they do not require an added curing agent and they develop less gas on curing.

One line of attack on the problem of better resins is through a study of catalyst systems and processing methods as applied to unmodified phenol-formaldehyde condensates. A resin has recently become available that can withstand temperatures of about 500°F. for 100 hours and of 4500°F.

for short periods. Another line of attack is through modification of the phenolic resin by condensing a silicon compound and phenol with formaldehyde.⁵

Phenolic resins have strong competition here from various synthetic resins. They have the lead at present but whether they can maintain it as improvements are made in other resins remains for the future to answer.

Fibers

When high impact resistance coupled with very high heat resistance is required, glass fibers are widely used as reinforcement. It is common practice to apply one of several treatments that have been developed to improve the bonding between glass and resin.

Without proper bond between the two, the fiber is merely a filler and not a reinforcement. It is quite probable that the ultimate has not yet been reached as to quality of treatment of glass fibers. Special types of glass have been developed for use in fibers, and silica fibers are also used for reinforcement. In a 4500°F. burn-through test, a combination of essentially pure vitreous silica and high-temperature phenolic resin is reported to have been particularly resistant to heat. Thickness required for 100-second burn-through were as follows for three compounds.⁶

Silica Fibers	0.39 in.
Asbestos Fibers	0.47 in.
Glass Fibers	0.63 in.

Sisal fibers have found considerable acceptance. They are lower in cost than glass fibers, form compounds of lower specific gravity, and show impact strengths 80% or more as good as glass-reinforced compounds. Nylon and Dacron have been given much attention. At present they are used

only when the properties they impart warrant their additional cost. Glass-fiber compounds have a raw material cost of the order of \$0.60 to 1.00 per lb.

Compounding

Components other than resin and fiber are usually eliminated from the compound to insure a minimum of gas or vapor formation at the high curing temperatures. The compounds range from fairly easily-handled plastic masses to bunches of resin-coated fibers. Those of a more plastic nature may be made in a sigma blade mixer. One method of making molding compound with little plasticity is to draw glass roving through a solution of resin or through molten resin and then chop into suitable length. Another method is to chop glass roving and simultaneously spray the fibers with resin and deposit them on a preform mold. Security restrictions probably withhold interesting recent developments in this field.

Chemical Resistance

The chemical resistance of phenolic-glass plastics depends upon the formulation and processing of the plastic and the concentration and temperature of the chemical solution. In general, molded parts react as follows:

Weak acids	Good
Strong acids	Decomposed by oxidizing acids
Weak alkali	Good
Strong alkali	Poor
Organic solvents	Good

Reaction with an alkylene oxide and alloying with an epoxy resin or a furfural alcohol resin are modifications designed to improve resistance to alkali.

MOLDING

Hot Molding

Phenolic compounds are commonly shaped by compression molding or by transfer molding. Injection molding, used widely with thermoplastics, is not generally satisfactory. The material tends to set up in the wrong places.

In molding compounds with high fiber content, it is preferable in most cases to preform the compound into shapes that require very little flow in the mold. This is to preserve the strength of the fiber and the fiber-resin bond.

Cure of the compound in the press is sometimes followed by a postcure, which helps to develop maximum strength and dimensional stability.

Compression Molding. The compound is charged to hot, matched, metal molds. Heat and pressure are applied to shape and cure the material. While the resin is only partially cured, the mold is opened briefly to release water vapor and other gases. This helps to prevent blisters in the molded parts. The compound charged to the press may be powder or preformed pellets or blocks. Preforms help in preheating the material and in handling the charge. Block preforms are particularly useful in the molding of large pieces.

Transfer Molding. The compound is plasticized in a transfer pot, usually located just above the cavity of the mold and connected to the cavity by an orifice and gate. Pressure applied to the plunger of the transfer pot transfers the compound to the closed-mold cavity. By this method, more intricate moldings can be made, inserts are located and held more securely, and the moldings are dense and uniform.

In a modification of transfer molding, a new type press

feeds powder from a hopper into a heated chamber, the temperature of which increases toward the discharge end. The compound is carried through the chamber by a screw and is fed intermittently into the mold cavity. Movement of the material, opening and closing of the mold, and discharge of molded pieces are synchronized automatically.

Automatic Presses. These are of obvious advantage to the molder. Substantial advances have been made in press design and in combinations of preheating equipment and presses. Economies effected through automatic molding reduce the cost advantage that molded thermoplastics have enjoyed over thermosetting materials.

Preheating. It is common practice to preheat the molding compound before charging it to the mold and so minimize the time required in the press. Heretofore, better results were obtained with preforms than with powder. Recent improvements in the preheating of powder now make it much more practical.

Molding of Powder Mixes. In isolated cases, dry mixes of unmilled compound have been charged to the mold. This is feasible only when the formulation of the compound is that of a very soft flow material rich in resin. With further improvement in the preheating of powder, this method may get further attention.

Cold Molding

One of the oldest methods of molding plastics is the cold molding process. The plastic is compressed and shaped in comparatively cold molds, then removed and cured by heating in an oven, following a predetermined schedule of increasing temperature. Synthetic resin, bituminous, and inorganic binders are used.

The synthetic resin is usually a phenolic. For this purpose,

a phenol-furfural resin gives very good results. The materials are not hot-rolled but are blended in mixers, such as the Lancaster or Simpson types. Sufficient volatile solvent or water is added to make the mass easily workable. A typical formula for cold molding compound is approximately as follows:

Asbestos floats filler	71.0%
Phenol-furfural resin	17.7
Furfural and dye	6.7
Alcohol, hydrocarbon oil, and wetting agent	4.6
	100.0%

Compounds so prepared generally contain only little more than one half as much resin as a hot-rolled compound with same filler.

The advantages of cold-molded compounds as compared to the hot-molded types are (a) lower compound cost, (b) higher output per molding press, and (c) good heat resistance and electrical properties in the molded parts. The finish is not as smooth as by hot molding and thin sections must be avoided in the design of the piece. Physical properties of cold-molded and hot-molded parts, using compounds having the same type of filler, are compared in Table 4.4.

TABLE 4.4. HOT MOLDING VERSUS COLD MOLDING OF PHENOLICS

	Hot-Molded	Cold-Molded
Specific gravity	1.84	1.95
Impact strength, Izod, ft-lb/in. notch	0.30	0.15
Tensile strength, psi	4200	3000–4000
Flexural strength, psi	7500	6000–7000
Heat-distortion temperature, °F.	330	Over 400
Heat resistance, continuous, °F.	450	500
Water absorption, %	0.20	0.61–0.65

The volume of production of cold-molded parts has declined considerably. Certain plugs, insulators, buttons, and other electrical parts are still made by that process. New developments in resins and techniques should provide an opportunity for renewed interest in this class of compounds.

USES

Table 4.5 lists some representative uses of phenolic molding compounds and gives an indication of the range of utility. Earlier, reference was made to production of compounds in degrees of flow or softness under heat. A given type of compound may be supplied in a different flow to each of several plants molding the same article because of the design of molding equipment, operating methods, or other factors. It is quite possible that the very versatility of phenolic molding compounds may be a handicap to them. A check of the catalog of one manufacturer indicated approximately 100 varieties of phenolic compounds. This must mean many short and unprofitable runs through the plant, large inventories, and extra development expense in keeping formulations up to date.

In spite of the high utility of the product, the production rate of phenolic molding compounds has been subject to substantial fluctuations. From 1950 to 1957, production of phenolic molding compounds varied between approximately 180 and 230 million lb per year, but the general trend has been essentially level, as will be seen by reference to Figure 4.1. In 1957 the production of all molding materials was roughly 1017 million lb, which represents an increase of 235 million lb or 30% over the 1950 production. Styrene polymers accounted for a large part of that increase, the 1957 production being 60% over the 1950 production.

TABLE 4.5. USES FOR PHENOLIC MOLDING COMPOUNDS

(1) Low-Reinforcement Group***Decorative, Mechanical,
or Electrical***

Ashtrays
 Automobile grilles
 Buttons
 Camera cases
 Distributor caps
 End plates for toasters
 Fan grilles
 Handles of various types
 Housings for instruments
 Housings for motors
 Instrument panels
 Insulators
 Knobs
 Mousetraps
 Phonograph cabinets
 Piano sharps
 Radio cabinets
 Switch housings
 Telephone hand sets
 Wheels and gears
 Wiring devices

Chemical-Resistant

Closures
 Milking machine parts
 Photographic developing tanks
 Rayon spinning buckets
 Storage battery cases
 Toilet flush tank floats
 Washing machine parts

Heat-Resistant

Automotive ignition parts
 Cooking appliances
 Diamond grinding wheels
 Electronic tube bases
 Heater plugs
 Protective relays
 Terminal blocks
 Thermostat casings
 Utensil housings and handles

Special

Bushings
 Printing plates
 Mottled moldings

(2) High-Reinforcement Group***Impact Types***

Bearings
 Cams
 Casters
 Covers
 Electric drill housing
 Gears
 Knobs
 Instrument cases
 Pulleys
 Rheostat hand wheels
 Switch bases
 Switch breaker arms

Heat-Resistant Types

Commutators
 Switchgear parts

Resin-Inorganic Fiber

Rocket parts
 Jet plane parts

Resin-Wood Chips

Cores for doors
 Structural parts for buildings
 Toilet seats

There appears to be a rather strong belief that the properties and economics of phenolic resins and molding compounds will keep them at about the same level for several years.

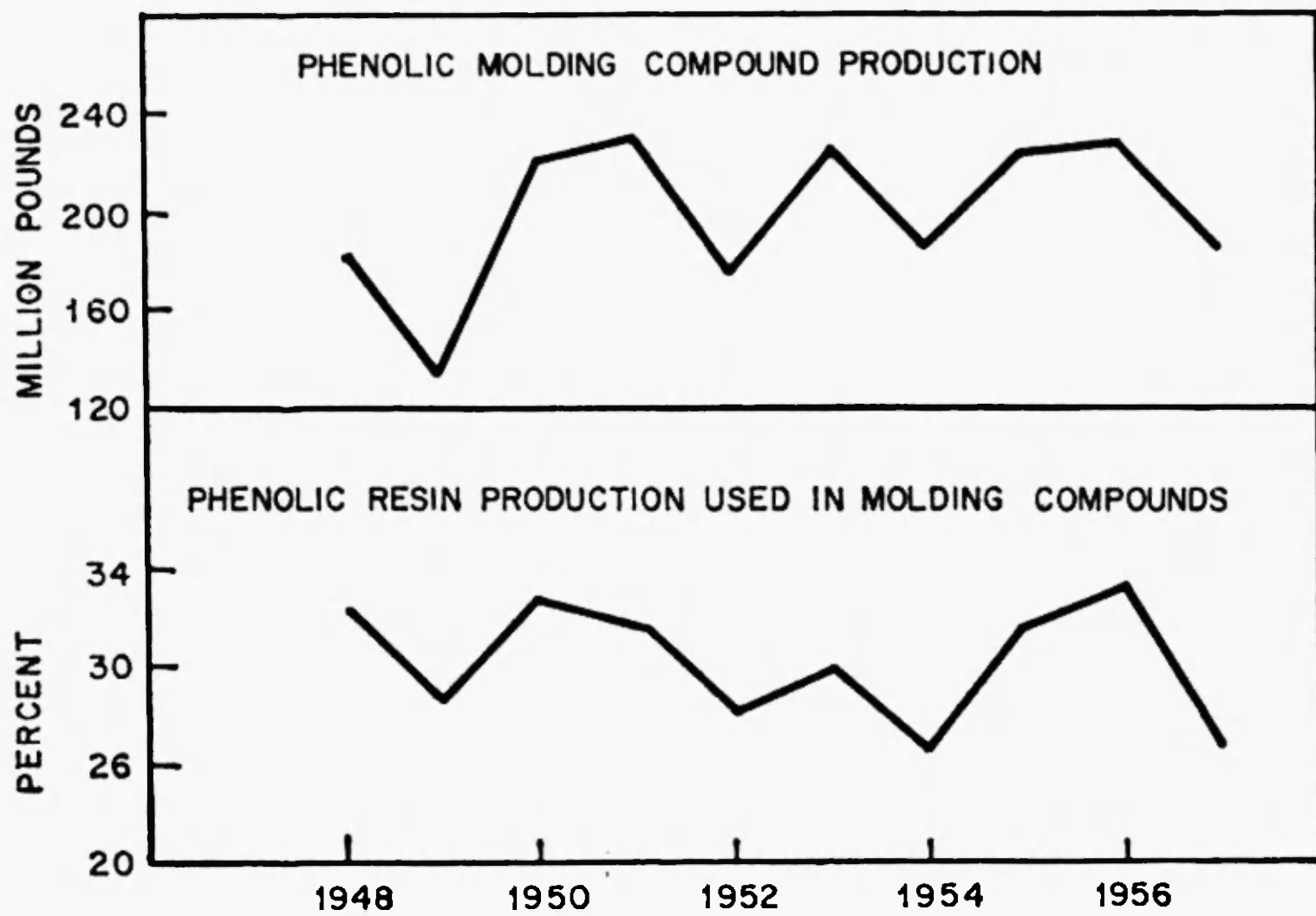
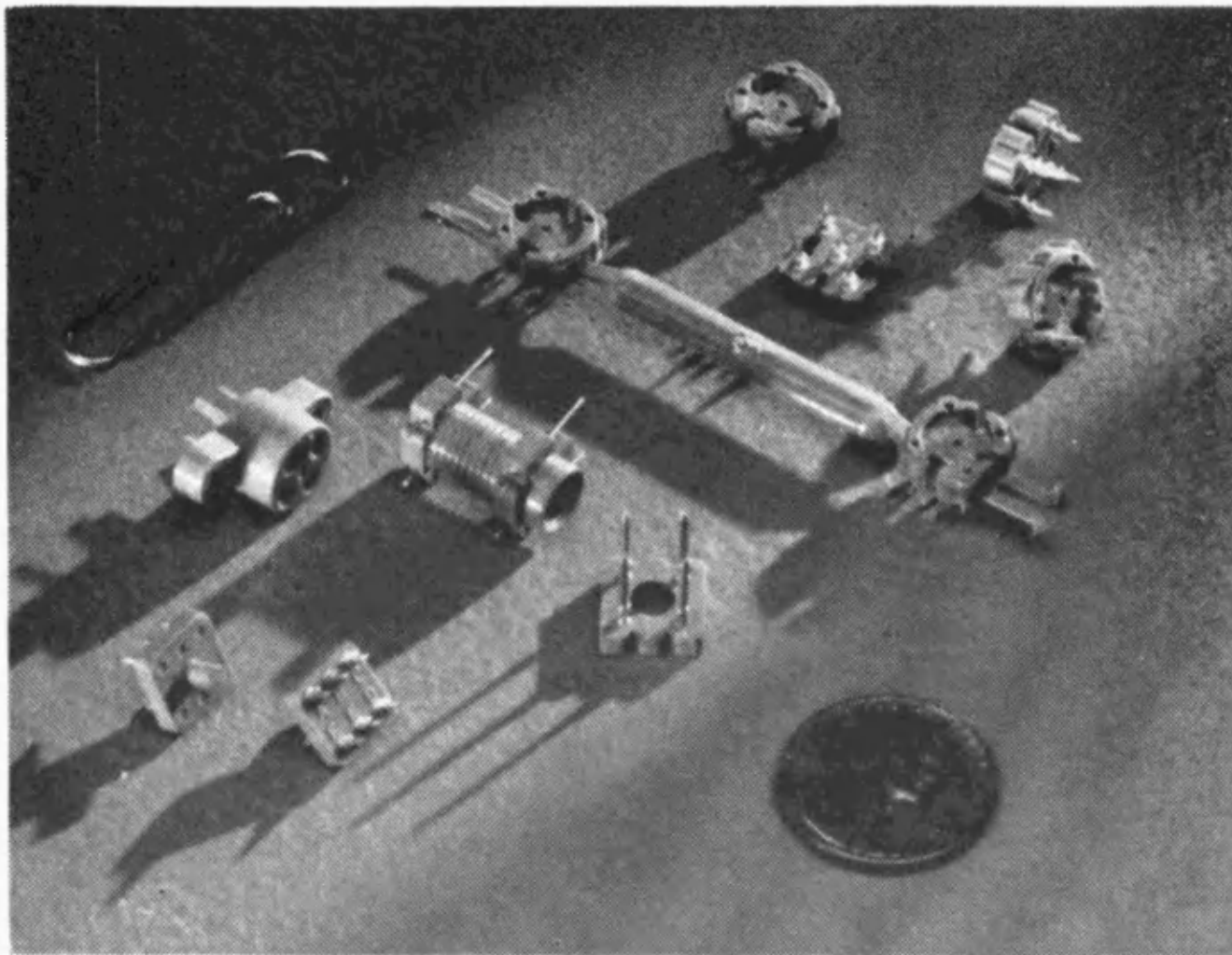


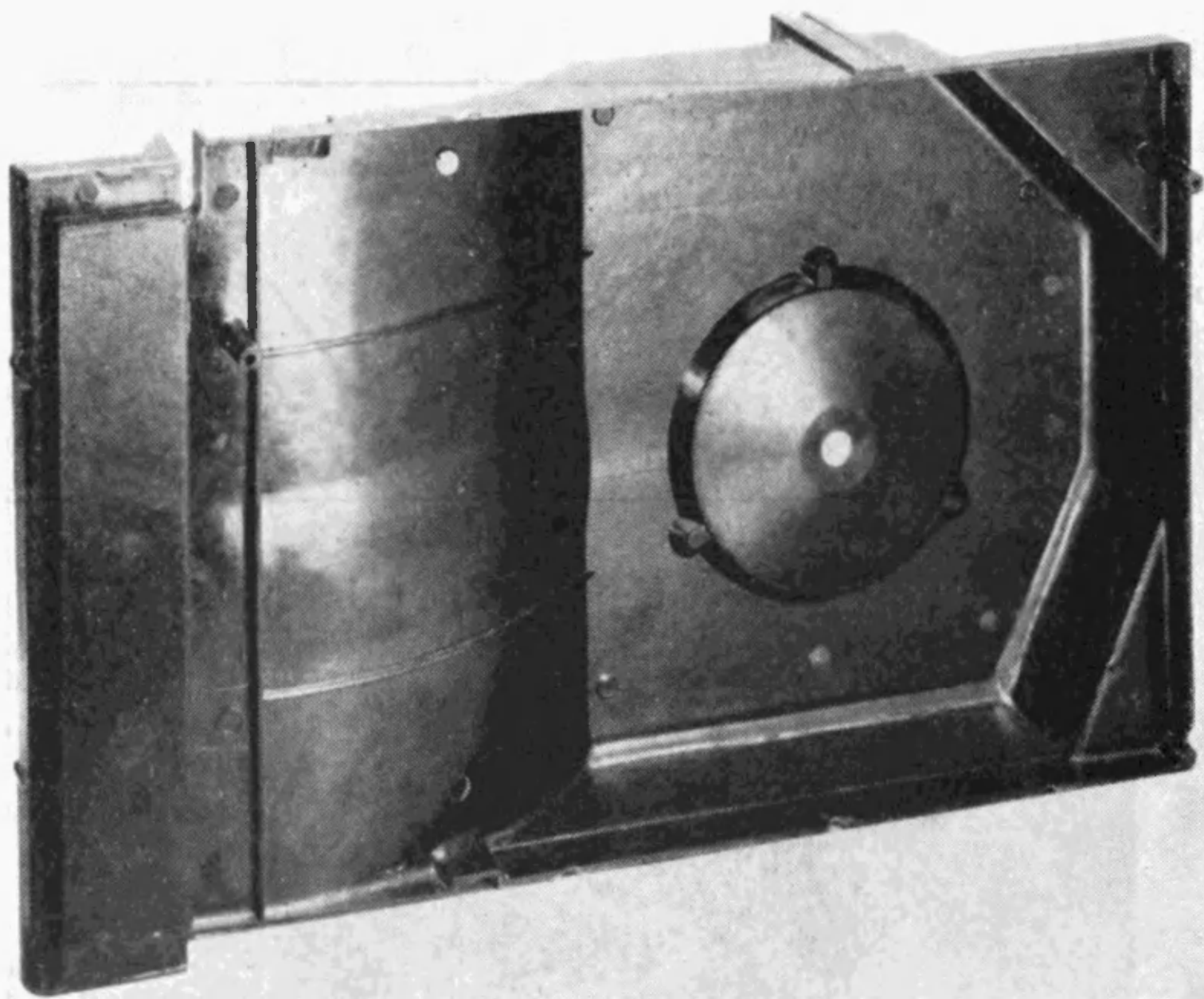
Figure 4.1. Phenolic molding compound production.



(Courtesy Hooker Chemical Corp.)

Figure 4.2. Parts molded of two-stage mineral-filled compound (parts molded by Grayhill Inc.)

The per cent of phenolic resin consumed in molding compounds has also varied, and it will be noted in Figure 4.1 that the peaks and valleys of the two charts are rather closely related.



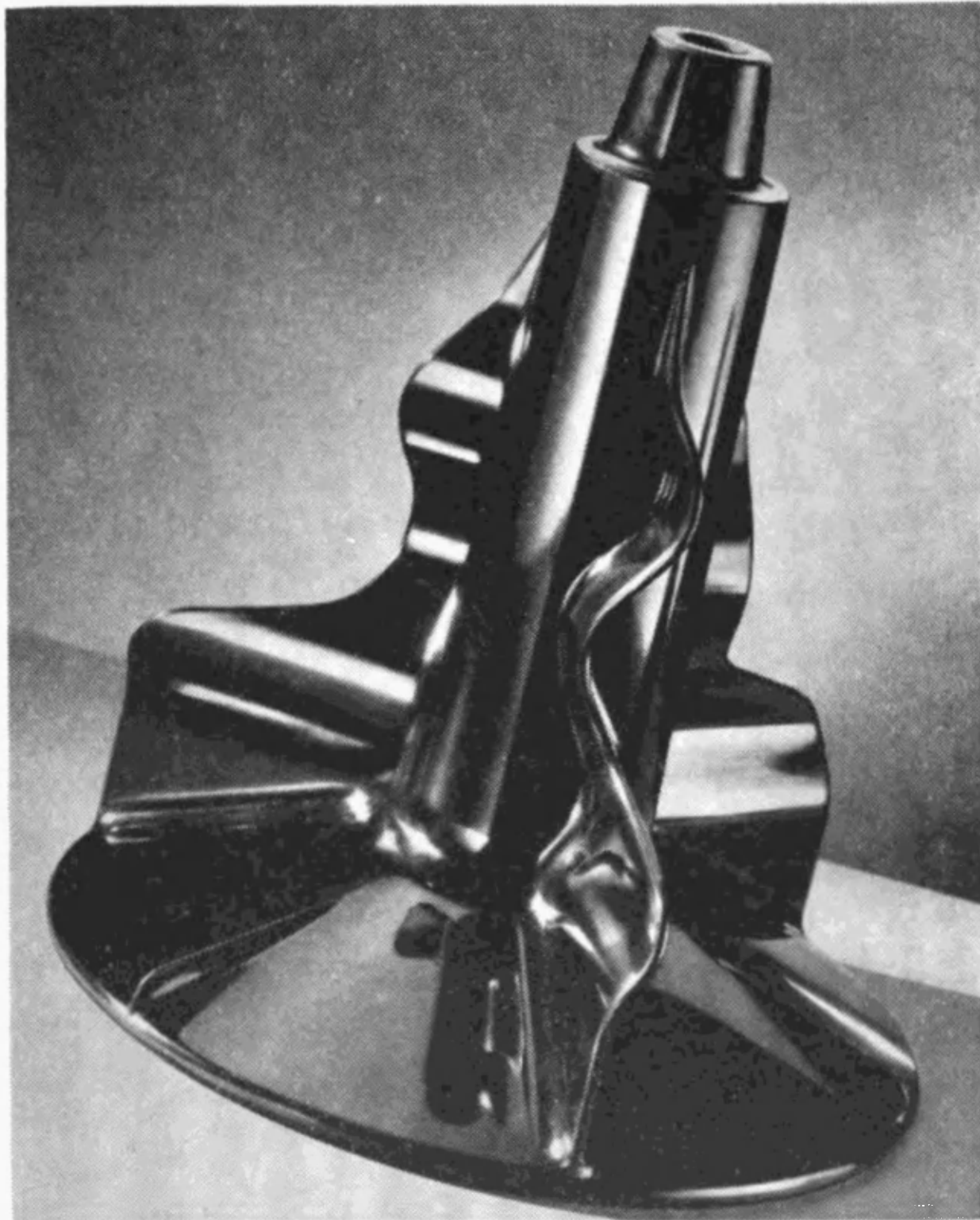
(*Courtesy Hooker Chemical Corp.*)

Figure 4.3. Blower housing for Emerson air conditioner (28 x 16 x 5").

A recent estimate of end use of phenolic molding compound indicated the major outlets to be as follows:

Electrical panels, switchgear, etc.	20%
Wiring devices	19
Utensil and appliance handles, housings, etc.	16
Closures	9
Automotive	7
Miscellaneous	29
	100

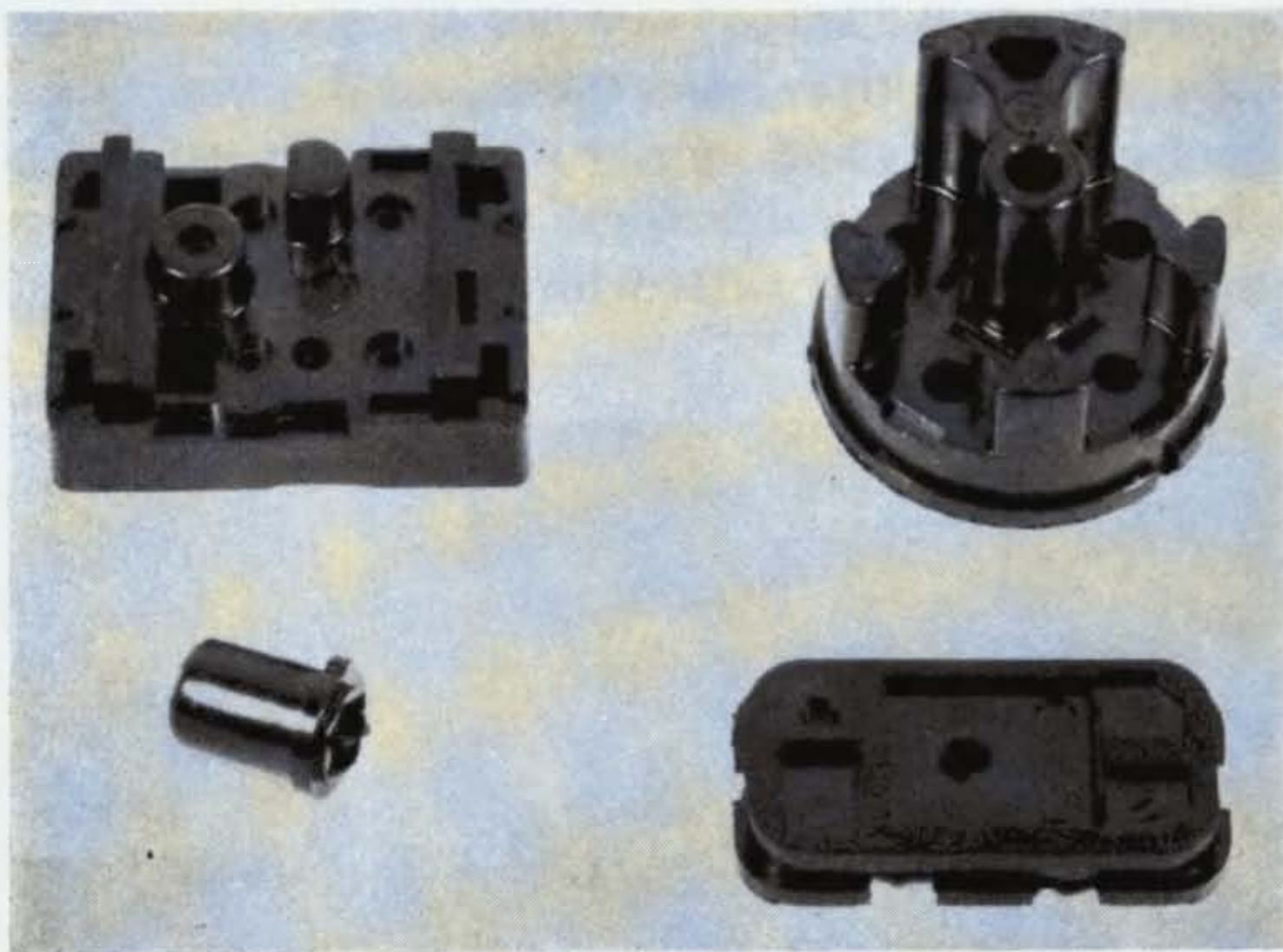
Figures 4.2 to 4.5 show examples of very small molded parts; a piece molded from a sisal-filled compound for mechanical strength and impact resistance; a molded part that requires mechanical strength, resistance to chemicals, and smooth finish; and parts with intricate detail.



(Courtesy Hooker Chemical Corp.)

Figure 4.4. Washing machine agitator.

In the following paragraphs, notes concerning some groups of uses are included with the thought that they may suggest additional applications.



(Courtesy General Electric Co.)

Figure 4.5. Intricate automotive and refrigerator parts automatically molded.

Chemical Equipment

Blower wheels for fume removal, material transfer, and the like have opened up a new field for phenolics. They are molded from general-purpose compound which is selected for rigidity, heat resistance, hard surface finish, lack of cold flow and creep, resistance to corrosive gases, low specific gravity, and price.

Tanks, towers, fume ducts, and other chemical equipment are molded from phenolic compounds by Haveg Industries, Inc. These go to the chemical, textile, petroleum, and metallurgical industries for use where chemical resistance is important.

This material is offered for continuous service up to 300°F. It is resistant to most acids, the weaker bases, and

most solvents. Oxidizing agents, strong bases, and a few other chemicals are not acceptable. A modified phenolic resin is used where resistance to wet chlorine gas is involved.

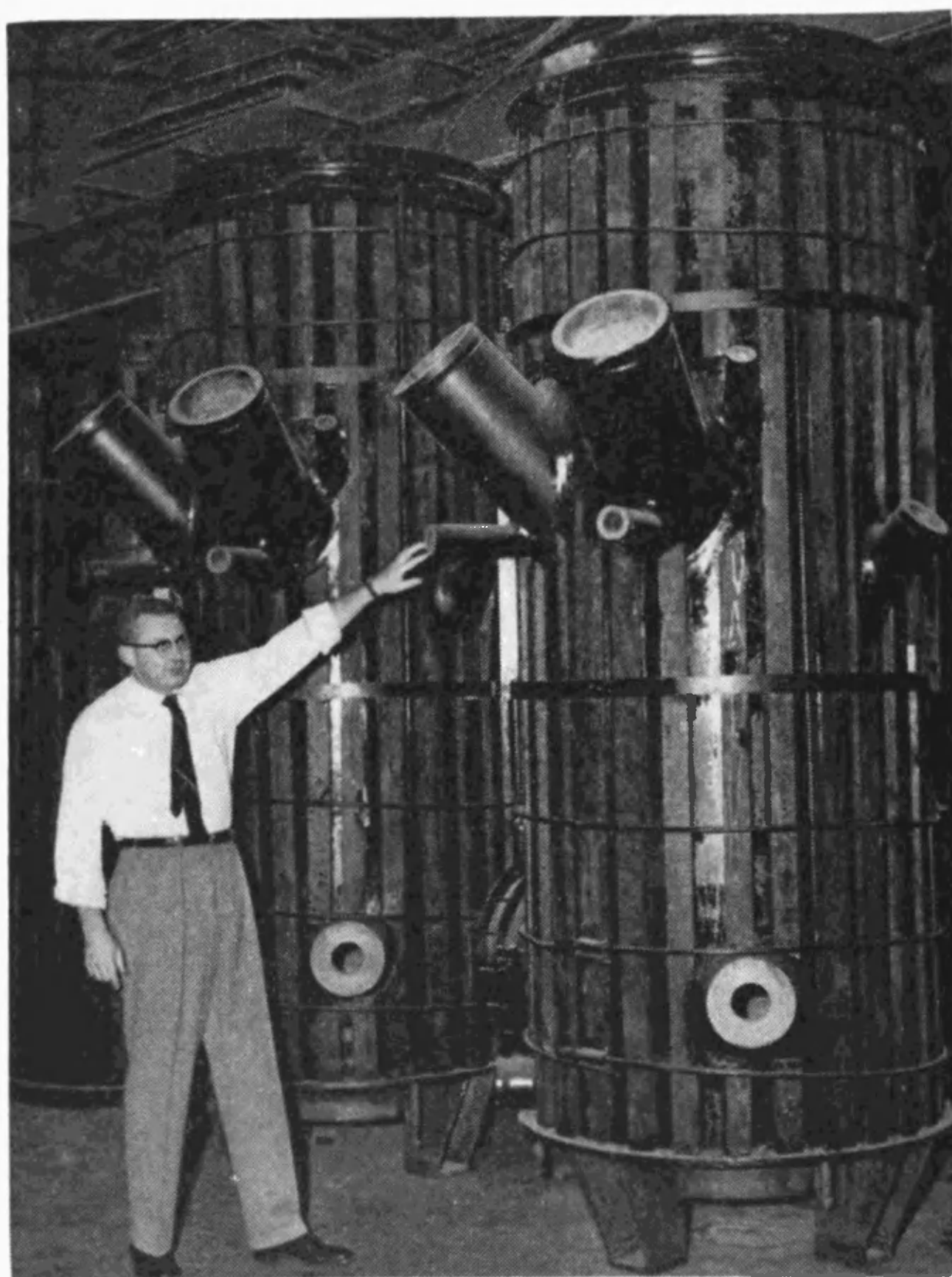
The cured material may be machined in various ways including threading. Cemented carbide tools are recommended. Properties of the molded phenolic material at two temperatures, as reported by the manufacturer, are as follows.

Temperature of Testing	78°F.	265°F.
Tensile strength, psi	2500	2000
Compressive strength, psi	12800	7000
Shear strength, psi	8600	6200
Compressive modulus, psi	5.0×10^5	1.7×10^5
Shear modulus, psi	1.1×10^5	1.7×10^5
Specific gravity	1.7	
Thermal conductivity, Btu/ft ² /°F./hr/in. of path	0.017	
Thermal coefficient of expansion in./in./°F.	1.1×10^{-5}	

Large parts such as seamless tanks up to 10 ft in diameter and 12 ft in depth are molded in light molds and cured in autoclaves.⁷

Still larger parts are produced in sections, which are later cemented together with a carbon-filled phenolic cement. Figure 4.6 shows a typical piece of chemical equipment.

Smaller parts are molded in conventional presses. An example is a filter plate, 24 sq ft in area.⁸ Another is the shell and baffle assemblies of heat exchangers.



(Courtesy Haveg Industries, Inc.)

Figure 4.6. Chemical corrosion-resistant equipment.

The increasing use of brackish water and sea water for process cooling has increased the demand for plastic materials to resist corrosion.

Electrical Equipment

Some molded parts commonly used in electrical equipment are listed in Table 4.5. In many cases, general-purpose

molding compounds are satisfactory. For more demanding service, electrical grades are supplied. To meet special requirements, further refinements are sometimes necessary.

Insulation. Good insulating properties in the molded parts require absence of moisture and of conductive impurities in the molding compound. Resoles are the preferred type of resin as they give off no ammonia during the cure. Fillers are frequently washed and dried before use. Compounding of the materials on the rolls is given extra attention.

Conductive Molded Parts. In some applications it is desirable that the molded part be electrically conductive. According to Canadian Patent 525,040, an anode for electroplating is molded from a phenolic resin-graphite compound. Cores for electrical use are molded from a phenolic resin-iron powder compound. The iron powder may be treated before molding to improve the electromagnetic and mechanical properties.⁹

Electroplated Parts

A few years ago very enthusiastic predictions were made as to potential use of electroplated molded parts for automobiles. These predictions have not yet been realized. Nevertheless, there is a small growth in this field. One of the most recent items announced is a housing for a microscope lamp which is molded and plated.

Furniture

Radio, phonograph, and television cabinets molded from phenolic compounds are familiar items. In this field phenolics must compete with thermoplastics on the one side and with sheet metal and wood on the other. The produc-

tion of molded plastic drawers for furniture has been one of the objectives of the plastic industry for a long time. It is expected that phenolic materials will have a share of the business but will not be predominant.

Phonograph Records

Early cylindrical phonograph records as made by Edison were formed from phenolic resin by a centrifugal casting method. With the adoption of the disc record, new methods were required and a laminated type was developed.

Many attempts have been made to use phenolic molding compounds, but they have two main disadvantages. The first is the relatively long time and high temperature required for curing the resin as compared to thermoplastic material.

The second disadvantage is that it is not practical to reuse rejected records or other scrap from phenolic compounds. Scrap from thermoplastics may be reground and reused, frequently with benefit to the quality of the compound.

The appearance of an occasional patent or article indicates a continued interest in the use of phenolic resins in records, but in recent items the phenolic resins are used only as adjuncts to vinyl resins. In one instance, the phenolic resin that is used is a phenol-terpene reaction product.

Pipe and Tubing

The potential market for plastics in this field is very attractive to the plastics industry, and predictions of plastic pipe sales of \$100 million in 1961 have been made. Many miles of 4-in. phenolic pipe have been extruded in Eng-

land.¹⁰ The process and product have been studied extensively in this country as well. However, of the substantial quantities of plastic pipe currently used, probably less than 5% is made from thermosetting resins.¹¹ Phenolic and epoxy resins make up the minority group. Part of the phenolics and probably all of the epoxy resins are used in laminated construction. The major reason for the more extensive use of thermoplastic materials is the greater ease of production and application.

Molded phenolic pipe is offered for use in chemical plants or where corrosive conditions exist. The specific gravity is near 1.7 or about one-fifth that of iron. Other properties were listed in the section on chemical equipment. Operating pressures recommended by the manufacturer (Haveg Industries, Inc.) are illustrated by the following.

	Maximum operating pressure—psi	
	60°F.	300°F.
3-in. Pipe	150	80
6-in. Pipe	90	48
12-in. Pipe	60	32

The usual fittings for piping are available in the same material.

An interesting method of making pipe from glass fiber and resin using a disposable rapidly rotating mold is described in U.S. Patent 2,773,287.

Printing Plates

Matrices and plates for printing appeared about 30 years ago. They were made from paper saturated with phenolic resin. More recently, matrices have been made from phe-

nolic molding compound. The matrices are then used to mold plates from plastic or rubber. This system is particularly useful in the preparation of advertising material that is to be distributed to many publications for simultaneous use. Phenolic plates have the following advantages:

1. Can be made to finer limits than metal stereotypes
2. Are much lighter in weight than metal plates
3. Are durable, runs of over a million have been made
4. Have no limitations as to fineness of screen
5. Can handle four-color work
6. Are resistant to rough handling and to corrosion in use or in storage
7. Require less ink.

Printing plates that can be postformed to cylindrical shape for use in rotary printing presses are made from a phenolic resin composition containing a small amount of a butadiene-acrylonitrile compound.¹² The use of a compound containing a copolymer of a conjugated diene and acrylonitrile or methacrylonitrile, vinyl chloride polymer or copolymer, and a phenolic resin that is compatible with the diene copolymer has also been disclosed.¹³

Present use of phenolics in printing is small, but the possibilities are there. Adequate promotion including the education of potential users to the possibilities should bring about a healthy development.¹⁴

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5. ADHESIVES

There are no accurate data on the total consumption of adhesives. The great number of materials used, multiple uses for many of the individual materials, complexities of formulations, and some production for captive use all con-

TABLE 5.1. ADHESIVE PRODUCTION (1954)

	Millions of lb
Synthetic resin types*	
Phenolics	134†
Ureas	181†
Vinyls	66
Nitrocellulose and related materials	13
	394
Natural gums and resins (not rubber)	26
Dextrin and starch	244
Animal glue	109
Others	187
	960

* Including solvents.

† Exclusive of amounts for laminating.

tribute to this situation. Data from the U.S. Census of Manufactures for 1954 presented in Table 5.1 indicate the order of magnitude of production of adhesives. Data for phenolic- and urea-resin adhesives do not include the amounts used for laminating. Corresponding data for 1947 are not complete, but there is evidence of an increase of production of 40% over the 7-year period.

GENERAL CONSIDERATIONS

Adhesive bonding is frequently preferred to other methods because it (*a*) makes possible the joining of shapes and materials that cannot be joined by other methods for reason of fragileness, thinness, or special shape; (*b*) permits economical use of relatively small pieces to form large shapes; (*c*) permits the use of expensive materials where their quality is essential for appearance, durability, or other property and the use of less expensive materials elsewhere for economy; (*d*) avoids the marring of surfaces by rivet, screw, or nail heads; (*e*) forms a vapor barrier; (*f*) distributes stresses in a manner not possible with other means of joining; (*g*) increases the scope of designing; and (*h*) permits lighter weight construction.

There is no universal adhesive. As Marra has written, the adhesive applicator would like to have a material with the durability of a phenolic, the quick set of hot animal glue, the ease of handling of polyvinyl, the clear color of a urea, and the cost of a soybean adhesive.

Durability

Bonds made with phenolic adhesives are regarded as the standard of durability. Properly prepared and cured, they

withstand very unfavorable conditions. Excellent results have been reported on 11-year exposure of phenolic-bonded panels to the weather in central New York state. These adhesives do not delaminate under prolonged exposure to hot or cold water, to alternating soaking and drying, or to alternating high and low temperatures. They resist the attack of microorganisms and of many chemicals. Wood may often be charred without destroying the adhesive.

Varieties

Adhesives are used as liquids, as melts, as unsupported films, and as impregnated tapes or tissues. Each form has its field of application.

The adhesives are supplied as liquids or as powders which are dissolved in a suitable solvent for application. Frequently they tolerate substantial additions of fillers or extenders, which reduce glue line cost and also control penetration of adhesive into the adherend. A wide range of compositions and properties are carefully adjusted to meet application conditions.

Resins Used

Phenolic resins are used in adhesives directly, as components of resin alloys, or after conversion into other types of resins. Epoxy resins are the major example of the last case. They are not included here. Phenolic alloys form a major part of phenolic adhesives and will be considered in detail on p. 94.

The phenolics are commonly prepared by alkaline condensation of formaldehyde with the lower monohydric phenols, resorcinol, or combinations of the two. The use of ammonia and amines as condensation catalysts has

TABLE 5.2. PHENOL AND RESORCINOL GLUES

Resin Characteristics	Type of glue				
	Phenol		Resorcinol-Phenol		Resorcinol
	Hot Neat	Press-Extended	Acid-Catalyzed	Intermediate Temp.-Set	Room Temp.-Set
Cures below 70°F.					×
Cures 70°F. and above				×	×
Cures 180°F. and above			×	×	×
Cures 240°F. and above	×	×	×	×	×
Low-pressure bonding				×	×
Light glue line			×		
Dark glue line	×	×		×	×
Good water resistance		×			
Waterproof	×		×	×	×
Heat-resistant	×	×	×	×	×
Plywood					
Water-resistant		×			
Exterior or marine	×		×	×	×

Adapted from The Borden Co. industrial gluing chart.

given very good results. Table 5.2 shows some of the characteristics of the adhesives made from those three groups of raw materials.

For bonding materials with some flexibility, phenol-formaldehyde resins may be a little too brittle. In such cases the use of a selected alkyl phenol for preparing the resin may contribute sufficient flexibility. If that is not adequate, the answer will generally be the use of a phenolic alloy.

Resorcinol resins are the only polyhydric type of phenol used directly in adhesives to any significant extent. Other materials such as bis-phenol are converted into epoxy resins before use in adhesives. Resorcinol resins are the only commercially important room-temperature setting members of the phenolic group. They also have the advantages of waterproofness and durability. Cost has restricted their use in many applications. This has led to the use of phenol-resorcinol-formaldehyde resins as a compromise between cost and performance.

It has been proposed to copolymerize phenols with a wide variety of other polymerizable materials. Phenol-urea-formaldehyde resins are probably the most important of this type. They are used to a greater extent as a binder than as an adhesive. Copolymerization of resorcinol, formaldehyde, and a partially condensed melamine-formaldehyde has been disclosed for the production of a cold-set adhesive.

Problems

The principal disadvantage of these adhesives is their relatively short storage life before application. This is particularly true of those made from the lower monohydric phenols. Storage life can vary widely with the formulation

of the adhesive, the amount of filler added, and other factors. The following data are illustrative:

Temperature of storage	40–50°F.	90°F.
Powdered adhesive	3–6 months	14 days
Liquid adhesive	18 months	60 days

Resorcinol adhesives as usually prepared have a markedly longer storage life than the phenol adhesives.

Other adverse features are a tendency for phenolic adhesives to bleed through when open-grain veneers are used, the time requirement for assembly which creates a problem in high-speed production, and the dark color of the glue line which is sometimes objectionable when the parts bonded are light in color.

Curing

Phenolic adhesives other than the straight resorcinol type require curing at elevated temperatures and under moderate pressures. The time required for cure may range from a few minutes at 150°C. to 24 hours at 50°C. The time depends in part on the character of the adhesive and in part on the method of heating and the heat transmission of the adherend. Dielectric heating is useful when bonding materials such as wood with a low rate of heat transfer. Under proper conditions the glue line may be heated without bringing the whole mass up to temperature.

For fast-setting or low-temperature gluing, it is sometimes possible to apply a phenolic adhesive to one surface to be bonded and a separate-application catalyst to the other surface. On pressing the two surfaces together, there is rapid cure. These combinations of resin and catalyst cannot be handled by the normal premixing procedure

because of the very short pot life. The method is not applicable to all phenolic formulations and does not give its best results on high-density woods.

PHENOLIC ALLOYS

Alloys of phenolics with other varieties of resins form an important part of phenolic adhesives. The principal resins used are the epoxy, vinyl, elastomeric, and polyamide. Some of the blends are particularly adapted to elevated-temperature applications. Some are suited to the bonding of dissimilar materials. Alloys with epoxies and vinyls show good weathering. Combinations with elastomers are useful in many applications where flexibility is needed. On the other hand, they also tend to creep under continued stress.

Phenolic-Epoxy Blends

These blends are particularly useful for high-temperature adhesion. The properties of the bonds depend upon (*a*) the structures of the phenolic and epoxy resins; (*b*) the proportions in which they are used; (*c*) the addition of stabilizers and accelerators, and the method of curing.

The addition of chelating agents, selected organic acids, and other chemicals has been found to improve the retention of strength of the adhesive bond at high temperatures. Black and Blomquist¹ have contributed considerable data on this point.

Phenolic-Vinyl Blends

The more common types are prepared with polyvinyl formal, acetal, or butyral. Shear strengths of over 5000 psi

have been obtained with this type of adhesive. Heat resistance is generally good up to about 200°F. These adhesives are more flexible than epoxy adhesives and more rigid than phenolic-nitrile rubber blends. Comparative weathering tests have shown phenolic-vinyl and phenolic-epoxy adhesives to be superior to the other common alloy adhesives. These adhesives are better able to absorb stresses than a straight phenolic adhesive.

The polyvinyl-formal combination is tougher than the butyral type. The polyvinyl-acetal combination shows good strength, impact, and fatigue properties. Polyvinyl-butyral blends are useful in bonding plastics, rubber, and metals. They show good durability and electrical properties. Those qualities have led to their use for many years in coatings for electrical wires.

Frequently the phenolic component is applied to the metal surfaces to be bonded. Powdered vinyl resin is then sprinkled onto the phenolic film. The parts are contacted, and the adhesive is cured under heat and pressure to give a strong serviceable bond.

A combination of polyvinyl acetal, polyvinyl acetate, and a cresylic acid-formaldehyde condensate has been disclosed for use on high-silicon steel. It is said to have toughness, adhesion, elasticity, good electrical insulation in thin layers, and resistance to acids, dilute alkalies, water, and oil. Phenolic resins added to polyvinyl acetate emulsions improve moisture- and temperature-resistance of the film and reduce creep and cold flow. This addition does not sacrifice the advantages of polyvinyl acetate.

Phenolic-Rubber Blends

Adhesives prepared from phenolic resins and natural or synthetic rubber have been in use for many years. The

importance of these adhesives has increased with the more widespread use of adhesives for bonding metals, glass, and other hard-surfaced materials. The greater range of choice of components has also improved the position of these adhesives.

The addition of rubbery materials to the phenolic resin gives a strong adhesive with considerable flexibility, especially at low temperatures. The flexibility is obtained at some sacrifice of resistance to creep under continued stress. Engle² reported this type of adhesive to be considerably the best, in impact resistance at room temperature, of the four general types of adhesives that he considered suitable for use as structural adhesives. The superiority did not hold at -100°F .

Highest bond strength for structural applications is generally obtained by curing under heat and pressure. Several types of rubber are used in compositions of this type, nitrile and neoprene types being the most common.

In producing the phenolic resins for these alloys, alkyl phenols are frequently preferred because of the better compatibility of the resins. The use of oil-modified resins and phenolic resins modified by incorporation of cashew nut-shell liquid has been disclosed in patents. These give tougher and more flexible adhesives.

Nitrile Rubber. By proper selection of nitrile rubber and phenolic, alloys may be prepared that have important properties as adhesives. In general, the adhesives may be cured with or without the use of curatives. Storage life of the cements varies with the characteristics of the components and is usually longer when no curatives are used. Table 5.3 presents some data on representative cements made with two types of nitrile rubbers.

Phenolic-nitrile rubber adhesives are frequently marketed as a two-component system of liquid and powder which

are mixed just before use. Best results are obtained by heat curing. Curing agents and accelerators are added to the formulation to assist the cure. Representative curing conditions are 300 to 500°F. at 50 to 200 psi for 15 to 30 minutes.

TABLE 5.3. PHENOLIC RESIN—NITRILE RUBBER CEMENTS

Parts by Weight		
“Hycar” 1072x3	6.0	
“Hycar” 1042		6.0
Phenolic resin	24.0	24.0
Coumarone-indene resin	1.5	1.5
Methyl ethyl ketone	68.5	68.5
	<u>100.0</u>	<u>100.0</u>
Brookfield Viscosity in Centipoises		
Original	70	130
After 3 months	100	140
Bond Quality*		
<i>Steel to “Hycar,” Canvas Backing</i>		
Stripping force in lb/in.	90	40
Adhesion failure	Stock	To steel
<i>Steel to Steel (1 sq in. Overlap)</i>		
Shearing force in lb	930	910
Adhesion failure	Cement	Cement

* Cured 30 min. at 310°F.
Data from B. F. Goodrich Chemical Co. Bulletin.
Note: Shearing force of steel to steel was increased to 1000–1040 psi by addition of curatives to the formula.

The cured bonds show good strength at sustained temperatures up to 300°F. and withstand temperatures of 500 to 600°F. for short exposures. The proportions of the components vary with the requirements for mechanical strength, flexibility, adhesion to specific surfaces, and durability. A maximum for tensile strength has been shown to occur

at a composition of 90% phenolic resin and 10% nitrile rubber. These adhesives find use as structural adhesives and as binders for abrasives and other materials. They are well-adapted to the lamination of plies of different materials.

Neoprene Rubber. Adhesive alloys containing neoprene rubbers are also important. They are used for bonding metals, wood, and many plastics. They show good fatigue and impact properties. Resistance to water, oil, and hydrocarbons is excellent. Highest strength is obtained when the adhesive is cured under conditions similar to those used with the nitrile rubber.

These adhesives may be formulated for room-temperature setting. As an example, Thomson³ has described the preparation of solvent cements by the use of combinations of neoprene rubber with *para*-substituted phenols. The butyl-, amyl-, and phenylphenols are the types disclosed. The bonds are claimed to be very strong and tough and resistant to heat, solvents, oil, oxygen, and moisture.

Polyamides

Highly-branched liquid polyamides are prepared by condensation of polymerized vegetable-oil acids with polyamino compounds. On mixing these polyamides with heat-reactive phenolic resins, heat is evolved. On heating the product to 300°F. for 60 minutes or to 400°F. for 15 minutes, water is evolved, and the resin thermosets. The cured resin is highly resistant to solvents and chemicals.

The wetting of and adhesion to many surfaces is a very favorable feature. A wide range of properties is available through variations in formulation. Increase of polyamide content in the alloy improves flexibility, alkali resistance, and impact strength. Increasing the phenolic resin improves solvent resistance and hardness.

Alloys of nylon-type polyamides with phenol and resorcinol resins are reported to be satisfactory for metal-to-metal and metal-to-glass bonding, but few data have been issued. They have good potentialities.

APPLICATIONS

Basically, phenolic adhesives are used where strength and resistance to heat, moisture, and chemicals are especially important. The main outlet for phenolic adhesives is structural applications.

In addition to the unmodified resins from phenol, resorcinol, and combinations of the two, several types of phenolic alloys are important as structural adhesives. Their sales are not large at present, but they are growing, and they have good potentialities. Engel² considers the phenolic-epoxy, phenolic-rubber, and phenolic-vinyl alloys to have demonstrated all-around properties for structural use. Phenolic-polyamide alloys are relatively new but show good promise.

Table 5.4 shows the comparative performance of several types of phenolic adhesives with various adherends. Factors other than bond-strength value often have important bearing on the choice of an adhesive for bonding a specific material. Usually in selecting an adhesive for a particular application, it is necessary to reach a compromise on several bond properties or to emphasize one property at the expense of others.

Metal Bonding

Two factors, mechanical bonding and specific adhesion, are important in adhesive bonding. Penetration of adhesive into pores or interstices of the adherends provides the

mechanical factor. Specific adhesion applies to the forces between the adhesive and the adherend. Since the mechanical factor is essentially absent in the bonding of metals, it is obvious that the specific adhesion must be brought to its maximum. Cleaning of the metal surface before bonding becomes particularly essential.

Muchnik⁶ has studied the factors involved in preparing metal surfaces for bonding. Black and Blomquist¹ have described methods developed at the Forest Products Laboratory and used successfully elsewhere.

Adjustment of the Adhesive. It is particularly important that the adhesive be adjusted to the thermal expansion and the flexibility of the adherends. In some cases a filler is needed.

TABLE 5.5. METAL BONDING

Adhesive	Shear Strength, psi, at 76°F.	
	Aluminum	Stainless Steel
Phenolic-vinyl	4682	6394
Phenolic-nitrile rubber	3776	2599
Phenolic-epoxy	2984	3319
Phenolic-polyamide ("Versamid")	2500	—

Note: These are average values from several sources. Some individual values differ substantially from the averages.

Types of Phenols. Straight phenolic-resin adhesives are offered for use on any metal except those that are galvanized or electroplated. The bond strengths are satisfactory for many uses, and the adhesives are economical. Resistance to heat varies rather widely with the metal. Further research is needed to resolve this. Epstein⁹ has shown that bond strength of phenolic adhesives at elevated temperatures is improved by using a two-step process for curing the resin. Resorcinol adhesives have been used. In

a test of room-temperature bonding of aluminum, a bond strength of 1600 psi was obtained after a 1-day cure.

TABLE 5.6. STABILITY OF ADHESIVE BONDS ON ALUMINUM

Adhesive	Shear Strength* After 1000 hr at 350°F.	Creep at 25°F.	
		in./in. of t./hr	Stress Applied, psi
Modified phenolic	2024	0.000125	1700
Phenolic-nitrile rubber	1461	0.00369	420
Phenolic-epoxy	1390	0.000213	1700
Phenolic-vinyl	875	0.00205	663
Epoxy	540	—	—
Reference 5			

* Tested at 350°F.
Note: These are averaged values. Individual values may vary substantially.

Where high-bond strength and resistance to heat are essential, alloys of phenolics with epoxy resins, vinyls, or elastomers are to be preferred. Tables 5.5 and 5.6 present data on the performance of several types of adhesives.

Glass Bonding

Most of the introductory statements on the bonding of metals also apply here. Considerable attention has been given to the treatment of glass fibers to insure maximum strength in reinforced plastics. There is need for much more information on treatments specific to the use of phenolic resins.

Type of Phenolic. Straight phenolic bonds are too brittle for best performance in many applications with glass. The most durable bonds at present are obtained with modified phenolics in combination with polyvinyl butyral. Tensile strengths of 1500 to 5000 psi are obtainable. Oil-modified

phenolic resins and resins from *para*-substituted phenols of the type used in varnishes are useful here.

Phenolic-rubber alloys give good bond strength with somewhat more flexibility than other types. They also bond glass to rubber and glass to metal. Room-temperature setting adhesives prepared from phenolic alloys are sometimes used. As in other adhesive applications the bond strength is generally not as high as when the adhesive is cured at elevated temperatures.

In a summary of commercial adhesives for glass, Moser¹² heads his list with phenolic-vinyl and phenolic-nitrile rubber alloys and notes their good weathering quality.

Low-Temperature Use. One of the difficulties encountered in adhesive bonding of glass is a tendency for the adhesive to chip the surface of the glass as the temperature goes below about 0°F. Plasticizing the adhesive decreases the chipping, but this is generally at the expense of bond quality.

Plastics Bonding

Use of adhesives with plastics usually applies to the bonding of (*a*) a noncrystalline type to itself; (*b*) two different types of plastics; (*c*) a plastic to a nonplastic. Bonding of crystalline types of plastics is commonly done with heat rather than with an adhesive.

Crystallinity and polarity of the plastic adherends are particularly important to the bonding of plastics. Skeist⁸ has discussed use in the design of adhesives. In bonding plastics to nonplastics, adhesives made from resins with diverse make-up such as the epoxy resins and polyvinyl butyral have the best chance for success.

For bonding phenolic plastics, the phenol, resorcinol, and phenolic-epoxy adhesives are useful. Phenolic-nitrile

rubber and phenolic-vinyl butyral alloys bond phenolics and phenolics to other materials. The nature of these bonds is such that they absorb stresses better than do the straight phenolics. Resorcinol adhesives also bond acrylic, cellulose acetate, and nylon plastics.

Rubber Bonding

Phenol-aldehyde resins and rubber cements are two principal adhesives used for many years for the bonding of rubber. Each type has different but desirable properties which can complement each other. Recent developments in synthetic resins and elastomers permit the advantages of combination of the two to be realized much more fully.

Alloys of phenolic resins with vinyls, nitrile rubbers, and neoprene rubbers have a higher specific adhesion and more flexibility than straight-phenolic resins. Phenolic alloys are recommended for the bonding of rubber to itself and to plastics, metal, and wood. There is an opportunity for the use of selected phenolic adhesives in the simultaneous curing of rubber and bonding to wood.

Tapes. Various combinations of phenolic resins with other materials have been proposed for the production of pressure sensitive tapes. One example is a blend of rubbery copolymer and a compatible oil-soluble phenolic resin. Another example is a blend of phenolic resin and a polyamide that is a reaction product of polymerized vegetable-oil fatty acids and ethylenediamine.

Tire-Cord Adhesive. Improved bonding of textile fibers to rubber in the manufacture of tires is obtained by coating the fibers with resinous compositions. Resorcinol-formaldehyde condensates are among those used. Resorcinol is sometimes applied to the fiber, and paraformaldehyde to

the rubber compound. Condensation and bonding take place during the curing of the rubber compound.

Wood Bonding

Phenolic adhesives find their major use where moisture resistance and durability are essential. They withstand practically anything that does not damage the wood. Laminated wood resists fire in a manner comparable to solid wood. Booth and Maxwell¹¹ have reported excellent results on test panels bonded with phenol and resorcinol resins and exposed to the weather for 11 years. The tests are continuing.

Most types of wood can be bonded. Some are more difficult to bond than others. Examples of the latter are teak, yew and osage orange used in archery, dogwood used for textile shuttles, and ebony used in pianos.

Major uses of phenolics are the bonding of various types of laminates and the bonding of wood particles. There is limited use of phenolics in certain types of flooring. Resorcinol adhesives find use as household or hobby adhesives. Boats, outdoor furniture, sports equipment, and kitchen equipment are examples of applications. The resorcinol adhesives are supplied as two components which are mixed in the amount required just before use.

There are many other applications where phenolic adhesives could be used with excellent results if desired. That they are not so used is generally a matter of economics. Ease of application of other adhesives and lower cost swing the choice of adhesive to them unless the durability of the phenolics is needed.

Curing temperature can be reduced from the usual level for phenol-formaldehyde adhesives by the use of phenol-

resorcinol combinations or of acid-cured phenolics. Deterioration of the wood on aging of pieces bonded with acid-cured phenolics has been observed. This has been attributed to the acidity of the adhesive. The subject warrants further research.

Resorcinol adhesives have outstanding properties and are the only low-temperature setting adhesives which have maximum resistance to exposure. Alloys with polyvinyl acetate and with melamine resin have appeared.

Miscellaneous Bonding

Resorcinol resins bond well to concrete. Many adhesives fail there because of the alkalinity of the concrete.

An estimate made in 1954 indicated that 1¼ million gallons of cement prepared from phenolic resins and nitrile or neoprene rubbers was used annually in the bonding of soles to shoe uppers.

The following are examples of other phenolic resin-containing adhesives that have been disclosed: (*a*) phenolic resin and shellac; (*b*) phenolic resin, butadiene-acrylonitrile copolymer, and vinyl chloride-acetate copolymer; (*c*) phenolic resin and polyvinyl butyral; (*d*) phenolic resin modified with glycerophthalate and methacrylate resin.

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6. LAMINATES

Data from the U.S. Tariff Commission indicate a recent annual average production of 70 million lb of phenolic resins for laminating, exclusive of plywood and certain other wood constructions. There is some basis for belief that that figure may be low.

The term “laminate” covers a very wide diversity of materials and constructions. Laminates may be separated into two types: (*a*) a multilayer construction of fibrous sheets and resinous binder compacted into an essentially homogeneous whole and having facing sheets of the same or different material or (*b*) a sandwich construction of a relatively thick, low density core adhesively joined to thin, high strength facing sheets.

SOLID CONSTRUCTION

Laminates of this type are commonly made by impregnating sheets of base material with a thermosetting resin, heating to remove solvent or other volatiles and to advance

the cure of the resin somewhat, stacking the sheets in the desired shape, and bonding by curing the resin with or without heat and pressure.

Fibrous Base

The base material may be papers, woven fabrics, or nonwoven mats. Cellulose paper is widely used in laminates for electrical applications. Cotton fabrics are useful for gears and pulleys and for molded parts that are to be punched, threaded, or machined. Nylon base helps electrical properties. Asbestos and silica are needed for high heat resistance. Comparisons are made between the base materials in Table 6-1. Values obtained on commercially molded parts may vary somewhat due to the effect of design of the part and method of molding.

Resins

Most of these laminates are made with phenolic resins. The latter have an important combination of heat resistance, dimensional stability, resistance to creep under load, and adhesion to reinforcement. In special applications, silicone resins and a few other types are used.

The phenolic resin is usually a single-stage phenol-formaldehyde type. It may be modified with aniline to improve electrical properties or with cresol to improve punching quality of the laminate. Combinations of phenolic and epoxy resins show good heat resistant and strength properties and may grow in importance.

New varieties of phenolic resins are coming from laboratory developments. Better catalyst systems and processing methods for making the resins and better curing techniques make them superior to previous types in both mechanical

TABLE 6.1. LAMINATES MADE WITH VARIOUS BASE MATERIALS

	Paper	Fabric	Asbestos	Glass Fabric	Nylon
Impact strength, Izod (ft-lb/in. of notch)					
Lengthwise	0.25-0.66	1.25-2.10	0.6	4.5-6.5	3.0
Crosswise	0.22-0.55	1.00-1.90	0.6	3.5-5.5	2.0
Compressive strength (thousand psi)					
Flatwise	22-36	35-39	38-40	38-70	Abt.
Edgewise	19-23	23-25	17-21	9-25	20
Tensile strength (thousand psi)					
Lengthwise	10-20	11-14	10-12	16-37	8.5
Crosswise	8-16	9-10	8-10	11-30	8
Mod. of elast. in tension (hundred thousand psi)					
Lengthwise	9-19	9-12	17-25	18-23	4
Crosswise	8-14	8-9	15-16	12-20	4
Mod. of elast. in flexure (hundred thousand psi)					
Lengthwise	9-18	9-11	16-23	13-17	6
Crosswise	8-13	8-9	14	10-15	5
Rockwell hardness (<i>M</i>)	75-120	103-105	103-111	95-120	105
Specific gravity	1.30-1.45	1.33-1.36	1.70-1.72	1.5-1.9	1.15
Thermal coef. of linear expansion × 10 ⁵	2.0	2.0	1.5	1.0-1.8	
Thermal conductivity (cgs system) × 10 ⁴	2.7	7		7-12	
Heat resistance (max. continuous, °F.)	200-250	225-250	275	275-400	165
Water absorption (¹ / ₈ -in. sheet, %)	0.75-3.30	1.30-2.50	0.95-2.50	0.30-2.0	0.40
Dielectric strength, v/mil*					
Short time	425-550	360	160	185-600	450
Step by step	290-400	220	95	160-450	300

* Dielectric data applicable to electrical grades only.

strength and heat resistance. They have a specialized use today but more general use may be expected in the future.

Facing Sheets

These may be selected for their decorative or utilitarian value. Materials used include copper, steel, aluminum alloys, cork, natural and synthetic rubbers, vulcanized fiber, and films of polyester and cellulose acetate.

Molding

Laminates of this type are molded into tubes, rods, sheets, and shaped forms. Many laminates are formed in molds under pressures of 1000 to 1500 psi. There has been considerable adoption of methods using pressures of under 400 psi. In some instances, the uncured laminate is held against a cavity mold by a pressure bag, a rubber plunger or the like. Under those conditions, the pressure is less than 50 psi. Low pressures benefit mechanical strength by minimizing breakage of fibers and sweating out of resin from the base material. Also, less expensive molds are required.

Prepreg

Continuous sheets of reinforcing material are saturated with resin, partially cured, and made into rolls for subsequent molding. This is known as prepreg and has been used for some time.¹ New developments in resins and reinforcing fibers have broadened the field of application of prepreg. This method gives better uniformity of distribution of resin and of cure but at the same time lack of flow of material in the mold limits application somewhat.

Postforming

This is a process in which cured phenolic laminates are heated at just below the blistering point until pliable. They are then quickly shaped in a wood, metal, or phenolic mold. Laminates designed specifically for this purpose are available. Rather intricate shapes are made and, with proper fabrication of the sheets, substantial savings in production costs are possible.

SANDWICH CONSTRUCTION

The type of laminate more generally recognized as sandwich construction is composed of a relatively thick, low-density core to which are cemented thin, high-strength facings which carry the load. A major characteristic of good construction is high strength and stiffness in proportion to weight. Cost reduction and good thermal and/or vibrational insulation are also important features.

Cores

The core material may be honeycomb or expanded plastic. Honeycombs are usually made of paper, metal, cotton duck, or glass fiber. Weight, strength, insulating value, rigidity, and cost are balanced in selecting the material. Fibrous materials are generally impregnated with resin, usually phenolic.

Foamed or expanded plastics have come into considerable use as cores. Phenolic resins are frequently used for this. Foam cores may be cut to shape and glued to the face sheets or the latter may be put into position and the plastic foamed in place. This aids in forming complex laminated

shapes. In some cases, a plastic foam is formed within the pores of a honeycomb to give additional strength.

Facing Sheets

Reinforced plastics are the most important materials. Phenolic resins compete with polyester, epoxy, melamine, and urea resins as bonding agents. Other plastics, wood veneers, and sheet metal are also useful as facing sheets.

Gementing Material

Phenolic resins, including some resorcinol resins and modified vinyl-phenolic resins, are important adhesives for joining cores to facing sheets.

APPLICATIONS

There are three main groups of laminates in use today: general industrial laminates; tooling and constructional laminates; and temperature-resistant laminates. Representative uses are listed in Table 6-2.

General Industrial Laminates

The laminates included in this group are usually of solid construction. The core and facing sheets may be of the same or different materials. Supplementary notes on some of the uses are given in the following paragraphs.

Bearings. Production details are disclosed in a number of patents. The base material is usually cellulose or asbestos and the binder is phenolic resin. In some cases graphite or other lubricant is added to the composition to make it self-

TABLE 6.2. APPLICATIONS OF PHENOLIC LAMINATES

General Industrial Laminates	
<i>Automotive</i>	
Bearings	Transmission parts
Insulation for switches	
<i>Aviation</i>	
Antenna masts	Propellers
Piston heads for shock absorbers	Pulleys
<i>Chemical Processing</i>	
Bubble caps	Plating barrels
<i>Electrical</i>	
Armature wedges	Printed circuits
Channels	Radar panels
Condenser seals	Switchboard panels
Power fuses	Terminal blocks
<i>Furniture</i>	
Desk tops	Table tops
<i>Paper Mill Equipment</i>	
Doctor blades	Table roll covers
Suction box covers	
<i>Refrigeration Equipment</i>	
Breaker strips	Door liners
<i>Ships</i>	
<i>Sports</i>	
Bowling pins	Skis
<i>Telephone Equipment</i>	
Relay spool end plates	Switchboard panels
Tooling and Constructional Laminates	
<i>Dies and Tools for Forming Sheet Metal Parts</i>	
<i>Sandwich Construction</i>	
Structural elements with honeycomb or expanded plastic cores for boats, ceilings, doors, floors, aircraft parts, packaging, drawing boards, etc.	
Temperature-Resistant Laminates	
<i>Parts for Missiles and Supersonic Aircraft</i>	

lubricating.^{2,3} Bearing retainers made of cotton fabric-phenolic resin laminate are said to be longer wearing at high speeds.

Containers. Phenolic laminates are used in the construction of chrome plating barrels. The solution is warm and highly corrosive and provides a good test of the chemical resistance of this material under corrosive conditions. In view of this and the good service given by other phenolic materials under corrosive conditions, it would seem that more use could be made of phenolic laminates for containers.

Electrical Equipment. Use of homogeneous laminates for panels, terminal strips, and the like are common. There are also numerous applications for laminates having facing sheets of special material. One example is the end plate for a telephone relay spool, which is made of phenolic laminate core and a "Mylar" facing sheet. Another example is electrical condenser seals, which have a facing sheet of rubber.⁴

Gears. Both laminates and molding compounds are used in the production of gears.⁵ The laminated type is stronger and its machining quality is better. Millions of such gears have been produced, ranging from gears for electric clocks and timing gears in automobiles to ten inch face gears in rolling mills. Operation in automobiles for the equivalent of 200,000 miles has been reported. They outwear metal at a ratio of about 3 to 1 and cost less.

Pipe and Tubing. High mechanical strength, chemical resistance, and dielectric strength are characteristics of the material. Tubes are made in diameters up to 15 inches and with wall thicknesses up to 2 inches. In most cases, production has been confined to a maximum length of about 6 feet. On the other hand, the continuous production of pipe from laminations of glass fabric and phenolic resin has been disclosed.⁶ A large part of the production of

laminated tubing is used in the electrical industry. Some is also used in chemical and gas lines where conditions are corrosive to iron and steel.

Punch Stock. Many small parts for electrical and other equipment are produced more economically by punching from cured laminated sheet than by forming individually. Laminates for this purpose are made in various thicknesses and in sizes up to 49 x 108 inches. Kraft, rag, and alpha-cellulose papers are commonly used. Stocks are designed for either cold punching or hot punching. Phenolic-paper laminates with a facing of copper have been very successful in radio construction and are being extended to other fields.

Tooling and Constructional Laminates

This group of laminates has become increasingly important in recent years. Aircraft, building construction, and small boats have been particularly active fields. Volume-wise this is the most important of the three application areas as an outlet for laminates but it is also the least important for phenolic resins.

Boats. The principal application of laminates made with phenolic resins is as cores. Honeycomb, surface impregnated with phenolic resin, was used extensively in the construction of a Navy landing craft with very satisfactory results.⁷ This is good evidence of the sturdiness of such construction.

Buildings. Present use of phenolics is in the form of plywood, honeycomb cores for doors, and sandwich construction for curtain walls. The latter are frequently of multiple material construction.

Tools. The automobile and aircraft industries have used phenolics at times for stretch forms, either as castings or as phenolic caps backed up with phenolic foam. Phenolic laminates find essentially no application in the production

of dies and punches. The industry wants the dimensional stability and the strength at operating temperatures that phenolics can give but, at the same time, regards the heat-curing techniques necessary to get those advantages as an economic disadvantage.

There is a small outlet for phenolic resin in the production of honeycomb cores used in nesting fixtures. Phenolic laminates are also used successfully in the production of dimensionally stable master models. These are usually mahogany veneers and phenolic resin.

Temperature-Resistant Laminates

Developments in missiles and supersonic aircraft have opened up challenging opportunities for laminates. It has been said that 85% of a missile could be made of plastics if the proper types were available. Plastic parts for missiles are now substantial business dollarwise if not poundwise. Even though the emphasis is now on missiles, much of the technical information is also applicable to aircraft. Ultimately it should also benefit laminates for the more common applications.

Property requirements for this application are far more exacting than for any previous use. For example, laminates for missile construction must be able to withstand temperatures that would vaporize steel plus the blast generated by the tremendous speeds.^{8, 9, 10}

The newer phenolics are superior to other plastics in their combination of heat resistance, rigidity, and adhesion to reinforcing material. However, further improvement must be made if the targets set by the designers are to be met.

Resins. Details regarding the latest phenolics have not been revealed but they probably differ from older types in

combinations of components, catalyst systems, condensation conditions, and methods of curing. Evidence of improvement is offered from several sources.

A phenolic laminate with an ultimate flexural strength of 50,000 to 55,000 psi and a modulus of elasticity in flexure of $5\text{--}6 \times 10^7$ psi has been announced. Approximately 50% of its flexural strength is said to be retained after 5 hours at 700°F. (tested at 700°F.).

An unmodified phenolic resin for use in laminates is said to be able to withstand 500°F. for 100 hours and 4500°F. for short periods. There are other reports of laminates with flexural strengths of 80,000 psi and 85,000 psi when molded at 35 psi and 1500 psi respectively.

Fiber Reinforcement. Glass, silica, and asbestos are obvious choices for fiber reinforcement when high temperatures are involved. However, unusual conditions imposed on laminates for missiles has led to use of unusual combinations of fibers. For example, reports have appeared of tests on a ¼-in. panel made by high pressure lamination of alternating layers of nylon and asbestos impregnated with phenolic resin. One face of the panel was exposed to 2000°F. for about 18 min. before the temperature of the other face reached 300°F.¹¹ Using asbestos alone, the temperature was approximately 80° higher.

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7. WOOD PRODUCTS

Only about one quarter of the wood in a forest finds its way into the lumberyard. The quality of wood is decreasing with the disappearance of virgin stands. Many low grade trees are cut, with a resulting increase in knots and other defects in the products.

Gluing and resin bonding provide the means for utilizing available supplies of wood more fully, for upgrading the over-all quality of wood, for making use of wood processing waste, for widening construction possibilities, and for supplying material for applications for which wood in its natural state is not satisfactory.¹

Wood products other than the familiar boards and timbers and the various articles carved or machined from wood blocks have increased in importance in recent years. They include the following:

Plywood

Laminated wood

Impreg and Compreg

Particle board

Hardboard

Molded wood waste

These products have increased in importance because:
(a) they have superior qualities for many applications;

(*b*) they help to upgrade wood while the general trend of quality of lumber is downward; (*c*) they enable a larger proportion of the wood of a tree to be used effectively.¹¹

PLYWOOD

“Plywood” designates a glued and compacted assembly of layers or plies with the grain of one or more of the plies at right angles to the grain of the others. Construction may be all veneer or there may be a lumber core with cross-bands and facings of veneer. Face veneers are frequently chosen for decorative or utilitarian effect.

The major advantages are: (*a*) high strength-to-weight ratio; (*b*) ease of installation; (*c*) approach to equalization of properties along the length and width of the panel; (*d*) less change in dimensions with change in moisture content than in solid boards.

Grades and Types

Plywood is classified by grades and types. The type is determined by the moisture resistance of the glued joint and the grade by the quality of the veneers. There are commercial standards set up.

Primary classification is into exterior type and interior type. Currently about 30% is exterior and 70% is interior. Annual production is about 6 billion sq ft of softwood and 1 billion sq ft of hardwood plywood in terms of $\frac{3}{8}$ -in. material.

Adhesives

Phenolic resins perform satisfactorily in all plywood constructions. In practice, they are used mainly in exterior

plywood where moisture resistance is important. Urea resins are strong competitors in interior plywood, mainly on the basis of cost. Other synthetic resins and protein glues are used to a lesser extent.

Booth and Maxwell² have shown the durability of phenolic resins in their report on the results of eleven years of exposure of test panels. A move toward the use of phenolic resins exclusively in Douglas fir plywood was instituted recently. How complete the change will be remains to be seen.

Production of phenolic and urea resins for this use was reported by the U.S. Tariff Commission as follows:

	Millions of Pounds	
	Phenolics	Ureas
1954	35	80
1955	44	99
1956	51	109
1958	46	96
Average	44	95

Phenolics Used

Phenol-formaldehyde, phenol-resorcinol-formaldehyde, and resorcinol-formaldehyde resins are used. Resorcinol resins cure at room temperature but are the most expensive. Straight phenol resins are the least expensive and cure at the highest temperature. All require a catalyst to accelerate cure.

In most cases the phenolic resin is alkaline-cured. Acid-cured phenolics are used occasionally but there is still uncertainty as to the exact effect of various acids on the endurance of the wood.

Performance data for several types of adhesives are given

TABLE 7.1. COMPARISON OF VARIOUS TYPES OF ADHESIVES ON VARIOUS VENEERS SPECIES UNDER CONTINUOUS UNPROTECTED OUTDOOR EXPOSURE, Courtesy of The Borden Chemical Company, A Division of the Borden Company.

Resin: Method of Cure ^b :	Phenol- ^a	Phenol-	Resorcinol-	Resorcinol-	Resorcinol-	Urea-
	Form. (liq.) H.P.	Form. (powd.) H.P.	Form. (liq.) R.T.	Form. (liq.) I.T.	Form. (liq.) I.T.	Form. (powd.) H.P.
3-ply 3/16" Yellow Poplar						
<i>Plywood Shear Test^c</i>						
Dry Shear ^d	290 100	385-95	315-100	390-100	265-100	385-90
Wet Shear ^e	215-70	290-100	300-95	355-95	310-100	405-65
3½ Cycle Shear ^f	230-95	320-95	310-95	300-100	295-100	220-35
<i>Outdoor Exposures^g</i>						
5 years	2	0	0	0	0	50
10 years	2	0	0	0	0	TD
3-ply 3/16" Red Gum						
<i>Plywood Shear Test</i>						
Dry Shear	265 100	420 95	460-100	620 60	345-95	340 85
Wet Shear	220 85	375-95	460 95	475-55	345-60	395-90
3½ Cycle Shear	200 90	380-95	435-95	505 90	365-85	270-45
<i>Outdoor Exposure</i>						
5 years	0	0	0	0	0	40
10 years	2	0	0	0	0	TD
3-ply 3/10" Douglas Fir						
<i>Plywood Shear Test</i>						
Dry Shear	245 100	305 95	265 95	295-95	280-70	240-100
Wet Shear	220 70	275-65	230-95	295-85	255-65	200-90
3½ Cycle Shear	200-95	240-90	220-100	235-90	225-75	TD
<i>Outdoor Exposure</i>						
5 years	0	0	0	0	0	70
10 years	0	0	5	2	0	TD

^a Especially formulated for use on Douglas fir.

^b H.P.—Hot-pressed at 280°F.; R.T.—Room temperature at 75°F.; I.T.—Intermediate temperature of 140°F.

^c The 1st figure is shear strength in psi, the 2nd is the estimated % of wood failure. Each value is the average of 5 specimens.

^d Tested dry.

^e Tested wet after 48 hours of soaking in water at room temperature.

^f Tested wet after 16 hours soaking at room temperature, followed by 3 cycles, each consisting of drying for 8 hours at 145° ± 5°F. and soaking 16 hours at room temperature.

^g Per cent delamination of total glue-lines. TD represents total delamination.

in Table 7.1. Performance varies from wood to wood because of variations in the physical nature, anatomical features and chemical composition of wood.

Production of Plywood

Veneers and cores (if used) are brought to prescribed moisture content. Liquid adhesive is applied by a spreader to one of each pair of adjacent faces to be bonded. A waiting period between application of adhesive and pressing of the panel allows the adhesive to increase body by loss of solvent and by reaction.

Panels are then compressed, usually in hydraulic presses. Both cold and hot methods are used. Pressing is generally followed by a maturing or conditioning period.

Applications

Typical uses for plywood are listed in Table 7.2. Those in which exposure to moisture and weather is involved are the major consumers of phenolic resins. Notes on a few such applications follow:

Aircraft: Mosquito bombers and other English aircraft used in World War II and some United States gliders were of plywood construction.

Houses: All-plywood houses were exhibited at the World's Fair in 1939-1940. One was subsequently moved to a farm in New Jersey and is still in use. An all-plywood barn was erected on the same farm and standard silos were reinforced by a lining of exterior grade plywood. Fairless Hills, Pennsylvania, is a development of prefabricated plywood houses.

Boats: Molded plywood boats have been in use for years. PT boats for the Navy in the last war were plywood-hulled.

Racing boats of the hydroplane type have hit as high as 180 miles per hour, illustrating the punishment that plywood hulls can take.

TABLE 7.2. PLYWOOD APPLICATIONS

Industrial

Concrete forms

Plain

With phenolic impregnated overlays

Exterior wall sheathing

Exterior siding

Interior walls

Roof sheathing

Subflooring

Floor underlayment

Flooring

Curtain walls

Furniture

Face panels

Unseen stock

Drawer bottoms

Packing Cases

Domestic

Export

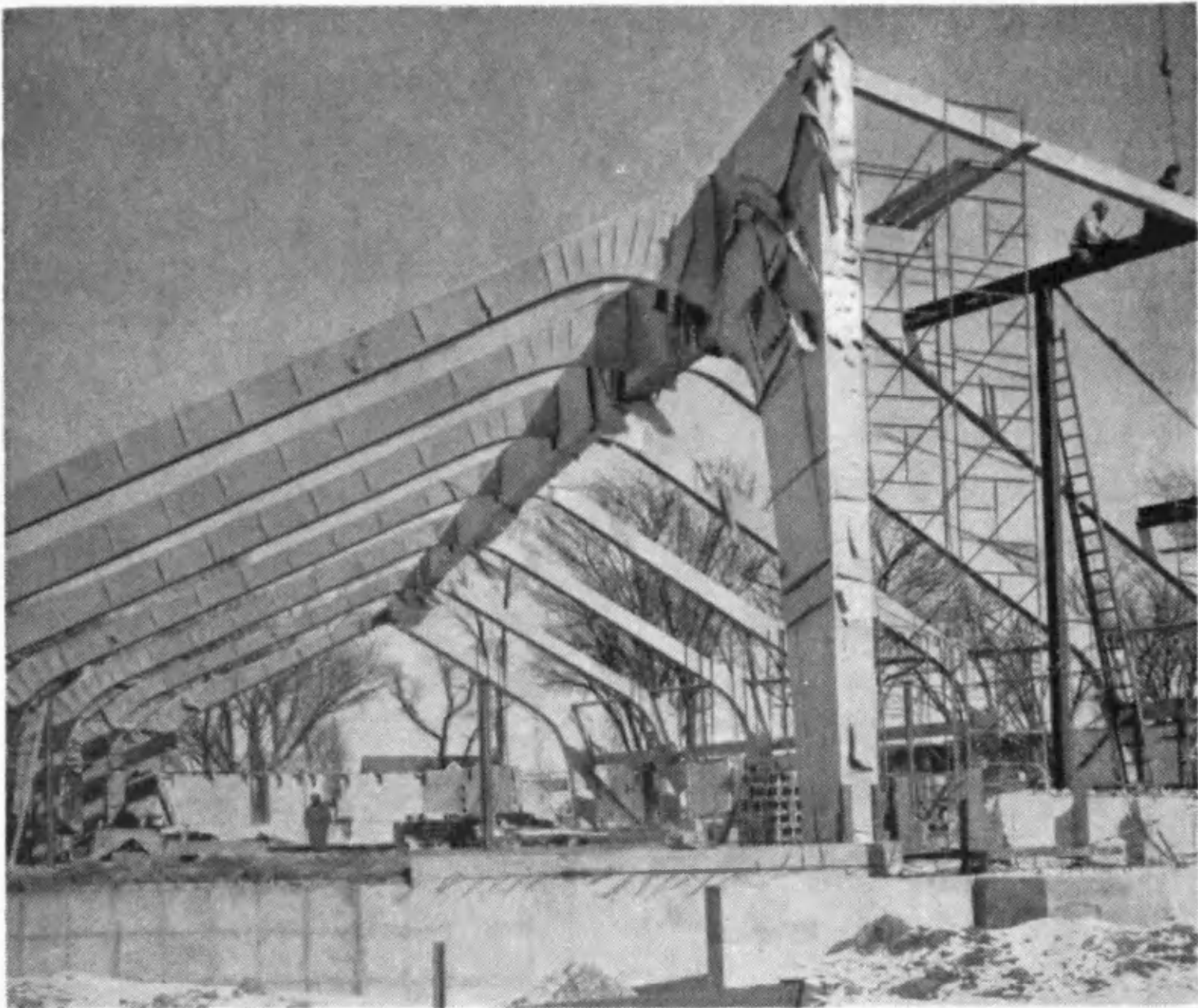
Curved Molded Plywood

Boats

Aircraft

LAMINATED WOOD

Laminated construction refers to two or more layers of wood glued together with the grain of all approximately parallel. The laminations may be of various species, num-



(Courtesy Forest Products Laboratory, U.S. Dept. of Agriculture)

Figure 7.1. Glued laminated arches (Our Lady of Peace Church, Madison, Wisconsin).

ber and thickness. Improvements in adhesives and methods have greatly increased the importance of lamination. The use of $2\frac{1}{2}$ tons of resin glue to bond 137 tons of lumber into arches for an arena 206 x 350 x 65 ft high is one example of the scale of application of phenolic adhesives. Figure 7.1 shows another example of large scale use of laminated arches.

Advantages

By itself, the simple act of gluing pieces of wood together does not necessarily improve strength properties. However,

glued-laminated construction does have important advantages:

1. The size and shape of many structural members now produced by lamination can not be duplicated as a single piece by sawing.
2. Even if large members can be sawed from a single piece, the quality of the member is generally improved if it is laminated. Knots or other defects may be eliminated or placed to minimize their effect.
3. Trees too small for production of large timbers and relatively short pieces of wood may be used effectively by lamination.
4. Desirable woods not available in large sizes may be utilized.
5. Strength values of duplicate members show better uniformity.
6. The use of expensive, high strength wood may be restricted in structural members to areas where most needed.

The main disadvantage in glued construction is a matter of economy. The adhesive adds substantially to the cost of the article. The adhesive cost in waterproof construction may be 10 to 15% of the total cost. Labor and supervision costs are generally somewhat higher.

Lumber

The lumber is selected according to the intended use of the laminate, the absence of defects, and the quality of the machined surfaces to be bonded. The kind of wood is chosen according to its mechanical properties and cost.

Adhesives

Phenolic adhesives are particularly important where moisture and heat resistance are required. Resorcinol adhesives are predominant where room temperature setting is required, as in production of large structures. Urea resins and casein glues compete with phenolics in other applications.

Assembling

The lumber is brought to a specified moisture content and then cut and fitted. Adhesive is applied and the parts are assembled, using jigs and forms to get the necessary contours. Flat assemblies are handled in presses. Large or irregular shaped laminates are held by various clamping devices.

Curing

If a room-temperature setting adhesive is used, it is only necessary to hold the clamped assembly for the required period. When higher temperatures are needed, high frequency heating may be used or the assembly may be transferred to a curing chamber. Marra³ has described a method whereby surfaces only of the parts to be bonded are preheated and bonding is only a matter of seconds after clamping.

Applications

Laminated wood has a wide range of application. Among the smaller items are skis, bowling pins, tennis rackets, bedposts, and table legs. In intermediate size are 2 x 4's for

building purposes, made by laminating 1 x 4's. Among the larger sizes are arches for churches, gymnasiums, and theatres; barn rafters that are continuous from foundation to peak; bridge timbers; and parts of ships.



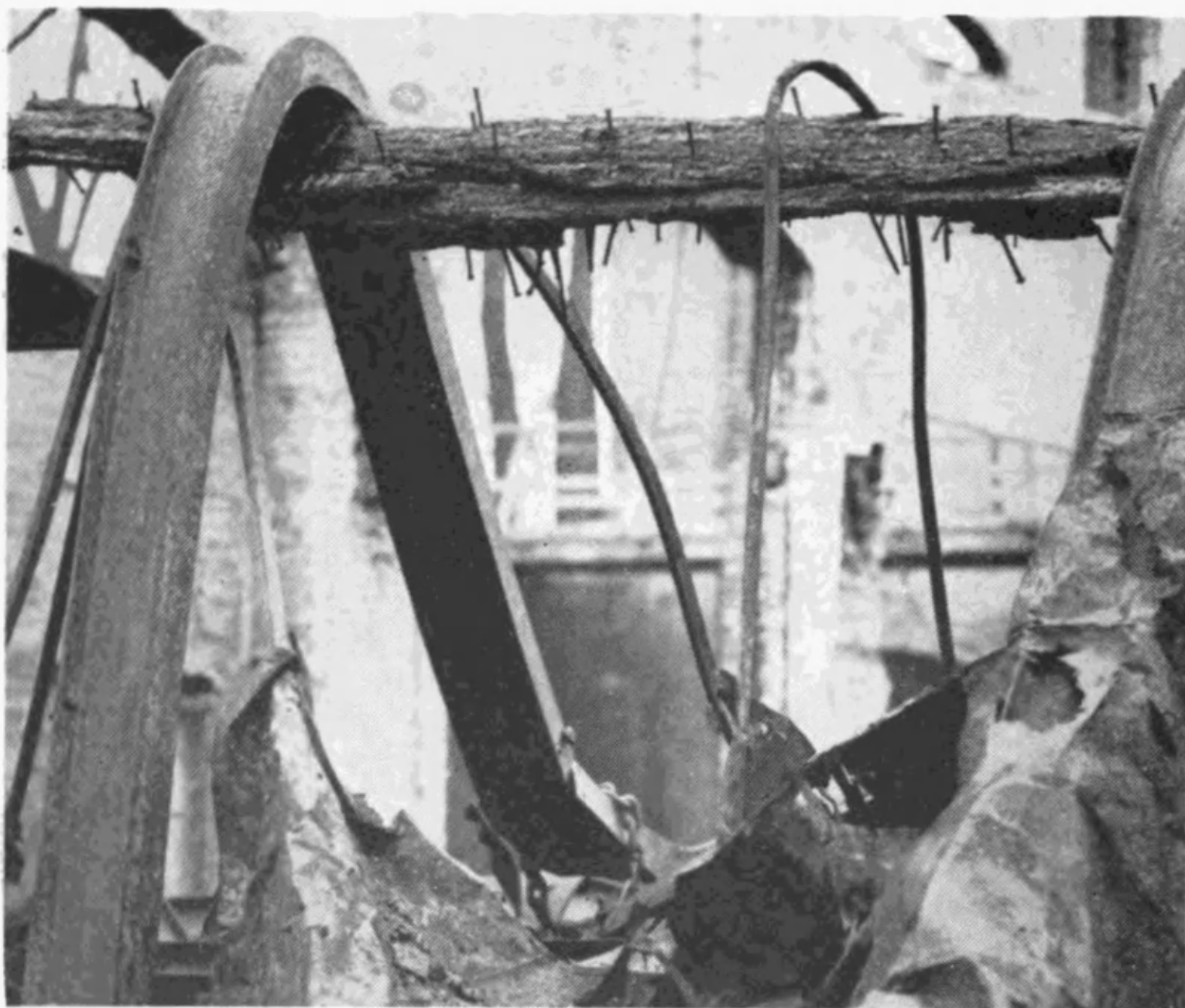
(*Courtesy Gamble Bros., Inc.*)

Figure 7.2. Laminated camel (U. S. Patent 2,426,345).

The minehunter "Bittern," which was launched early in 1957, offers an interesting example of the use of laminates in ships.⁴ Laminated timbers were used extensively throughout the major construction in combination with solid tim-

bers. Over 7000 lb of resorcinol adhesive was used for the lamination and other gluing.

Another interesting example of laminated wood construction is the ship fenders (camels) developed for the Navy during World War II. This fender, which is covered by U.S. Patent 2,426,345, is shown in Figure 7.2. The frames of the fender are wood springs laminated with Borden LT 67 resorcinol-phenol adhesive. The springs are able to close under lateral pressure and so cushion the impact between ships or between ship and dock.



(Courtesy The Borden Chemical Co., a Division of The Borden Co.)

Figure 7.3. Wood and steel versus fire.

In numerous instances it has been observed that wood beams in a building have resisted fire and continued to support the structure much longer than steel beams. The

latter quickly heat up to the sagging point, whereas it takes a substantial time for fire to burn through a large timber sufficiently to weaken it disastrously. This is shown rather vividly by Figure 7.3. With good phenolic adhesive and proper workmanship, a laminated timber should be at least as effective as a solid one.

IMPREG AND COMPREG

Veneers are impregnated with resinous condensate, dried, and heated to cure the resin. During the process, the condensate plasticizes the wood. When the cure is carried out without pressure the hard product is "Impreg." If the veneers are pressed during the cure, it is possible to compress the wood to a density approaching that of wood substance itself, the specific gravity of which is about 1.46. The very hard, dense, water-resistant product is "Compreg." Its hardness may be as much as 20 times that of untreated wood. The cost of resin-treated, compressed wood was estimated at 40 to 45 cents per lb in 1955.⁵

Resins Used

Alkali-catalyzed phenol-formaldehyde resins are the predominant type for this purpose. Phenol is generally used in this country but cresol is the usual raw material in Europe. Their products frequently show higher impact strengths. Urea resins require twice as much pressure for the same compression and the product is not as stable.

The condensate should be mainly in the phenol alcohol stage. It then diffuses into the wood structure faster and more completely. Reaction between polar groups of such condensates and hydroxy groups of the wood cellulose promotes water resistance in the product.

Substitution of alcohol for water as solvent for the phenolic condensate leads to higher impact strengths in the Compreg. Solvent cost is an unattractive feature.

Kind of Wood

Any kind of wood except the resinous pines can be used. The stronger the original wood the stronger will be the product. Yellow birch and sugar maple are probably the most popular.

Processing

Wood veneers are commonly used because faster and more uniform distribution of resin is obtainable. The veneers are impregnated with 25 to 35% of resin by weight of dry wood. Press curing of Compreg is similar to that of plywood. There is appreciable compression of the wood at 200 psi. Usual pressing conditions are: 1000 psi pressure at 300°F. for 30 min. per inch of thickness of the stack of veneers. The product is cooled below 200°F. before the pressure is released.

Working

Compreg is intermediate between untreated wood and metals in cutting and machining properties. Tools should be specially hardened. Compreg may be joined by gluing if the glazed surface is first removed by sanding. Phenolic resin adhesives are satisfactory.

Applications

Compreg was used during World War II for trainer-plane adjustable-pitch propellers, motor test propellers,

antenna masts, spar and collector plates, refrigerator blocks for ships, and tooling jigs.

Gurvitch⁶ estimated that a minimum of 1 to 1½ million lb went into cutlery handles in 1955. Picker sticks for textile looms, forming dies, gears, and molded desk legs are using increasing amounts of Compreg. There appears to be a more widespread use in Europe. A trend in the direction of replacement of fabric-reinforced plastics is seen by some. A Forest Products Laboratory report suggests that the best promise for the future lies in facings for plywood, possibly as a replacement for expensive hardwood plywood.⁵

SHAPED WOOD PARTICLES

Some parts of trees that can not be used for lumber or veneers and waste wood from wood-working operations are utilized in two commercially important processes. One is the production of synthetic lumber (composition board) and the other is the production of molded shapes.

Composition Boards

There are two general types in which synthetic resins are used. They are particle boards and hardboards. A third type of composition board, called softboard, is not included here as it offers no outlet for phenolic resins.

Composition boards do not equal good solid lumber in mechanical strength, machinability, and ability to hold screws. On the other hand, good composition boards are harder, have lower thermal conductivity, have fewer defects throughout their structure, and can be made to have higher dimensional stability. Properties of the three classes of composition boards are compared in Table 7.3. The

TABLE 7.3. GENERAL CLASSIFICATION AND PROPERTIES OF WOOD COMPOSITION BOARD*

Properties ↓	Class →	Hardboard (fibrous)		Special Densified	Particle Board		Softboard (insulation)		
		Untreated	Treated		Low Density ^b	High Density	Semirigid	Rigid	Intermediate Density
Thickness generally available, in		1/10-5/16	1/10-5/16	¼-2	¼-¾ ^c	1/10-¾	½-1½	¾-1 ^d	3/16-½
Specific gravity		0.88-1.04	0.95-1.15	1.35-1.45	0.40-0.80	0.80-1.05	0.02-0.15	0.15-0.40	0.40-0.80
Density, lb/cu ft		50-65	60-70	85-89	25-50	50-70	1.5-9	9-25	25-50
Thermal conductivity, Btu/sq ft/hr/°F./in.		0.80-1.40	1.50	1.85	0.40-0.80	—	0.24-0.27	0.27-0.40	0.40-0.80
Modulus of rupture, psi		3000-7000	7500-10,000	10,000-12,500	400-4000	3000-7500	—	200-800	400-4000
Modulus of elasticity in bending, 1000 psi		400-800	800-1000	1250	300-700	400-1000	—	25-125	90-700
Tensile strength, psi Parallel to surface		1000-3000	4000-5500	7700	100-1350	300-2500	—	200-500	800-2000
Perpendicular to surface		—	—	500	90-400	275-400	—	10-25	—
Compression strength (parallel to surface), psi		1800-6000	4200-5300	26,500	—	3500-4000	—	—	500-3400
Water absorption (24 hr.), % by wt.		3-18	3-13	0.3-1.2	5-50	15-40	—	—	—
Maximum linear expansion, % ^e		0.60	0.40	—	0.40 ^b	0.85	—	0.50	1.30

* Reproduced by courtesy of "Materials in Design Engineering."

^a Values given in table are approximate since they vary among different products depending on materials and manufacturing processes used.

^b Does not include extruded board.

^c The extrusion process is capable of producing thicker board.

^d Specimens up to 3 in. thick are made by lamination.

^e Expansion resulting from change in moisture content from equilibrium at 50% RH to equilibrium at 97% RH.

data are from a helpful review of composition boards by Riley.⁷

Particle Boards

Other materials have been used but at present wood is the outstanding raw material. Various scrap from forest, lumber mill, or factory is used. Bark and sawdust have only limited use. The wood is reduced mechanically to small pieces such as flakes, splinters, chips, etc. There is a trend toward the use of flakes of specified dimensions made from green wood, because of the strength and decorative value of the product.

The wood particles are blended with 5 to 10% of resin as a binder. A small amount of wax is frequently added to improve surface finish. The wood particle-resin mix is formed into boards by pressing into flat panels or by extruding and the resin is cured. Flat panels are usually carried to a density of 25 to 50 lb per cu ft. They are usually made in thicknesses of $\frac{3}{8}$ to 1 in. Extruded boards are produced in various shapes. One difficulty with extruded pieces is a tendency toward a weakness along the direction of extrusion. Facing sheets are frequently applied to correct this.

Resin Used. The binder for particle board must be low in cost, since the cost of the resin may be 25 to 50% of the total cost of the board. The resin must also have suitable viscosity for spraying onto the wood particles, high solids content to minimize drying time, rapid curing characteristic, and be capable of developing high strength. Many inorganic and organic materials have been studied for this use.

Phenolic resins have superior properties for use in particle boards for exterior use or other applications involving

hot or moist conditions. The resistance of phenolics to bacterial action and to chemicals is superior. Phenolic resins are excellent for high density boards and for the surface layer of three layer boards. By using a properly selected cresol or other alkyl-substituted phenol for making the resin, the board may be made more flexible. Resorcinol resins are excellent for strength and water resistance but are too expensive for ordinary use.

Applications. Flat panel boards are used as independent panels and as cores. As panels, they are used for walls and ceilings, for sub-floors and underlayments, kitchen cabinets, and sliding doors. By selection of particles decorative effects are obtainable.

As core stock, the following are typical applications:

- Tops for desks, tables, and chests
- Sides, backs, and shelves for bookcases
- Kitchen and restaurant furniture
- Doors for rooms and cabinets
- Headboards and rails for beds

The principal use for extruded particle board is as core stock, to which facings of wood veneer, plastics, or hard particle board are bonded by gluing. The extruded particle board then becomes an alternative for lumber or plywood. In thicker forms, this type of board is used to some extent as the core in building partitions.

Hardboard

The types of hardboard are the untreated, the treated or tempered, and the special densified. Typical properties of these three types are shown in Table 7.3.

Wood for this process is prepared by reducing mill waste to pulp chips and the pulp chips to fibers. The fibers are blended with 0.5 to 3% of resin and a small amount of

wax. The blend is molded and cured in a multiple opening press. Several variations of the process are in use. Press temperatures are commonly 350 to 400°F. Pressures vary with the density required in the hardboard but are usually in the range of 50 to 750 psi.

Treated hardboards are made by impregnating hardboards made by the above methods with drying oils and heating in an oven to cure. For the special densified type, the compression is carried to a high degree and the product approaches compreg in nature. These two types are produced in smaller volume than the untreated but are growing in use.

Resin Used. Lignin substances in the wood have a certain amount of binding action for the fibers under heat and pressure. However, the bond is not always adequate and frequently a supplementary bonding agent is added. Phenolic resins are well suited to this use. Moffitt and co-workers⁸ have described their use in the several hardboard processes.

Generally, liquid phenolics are used and the characteristics of the resin are varied with the hardboard process used and with the surface gloss, hardness, and stability desired in the hardboard. Patents disclose modification of phenolics with urea and with amines. Mixtures of phenolics with rubber latex, sulfite waste liquor, vulcanizable oil, polystyrene, and vinyl resins have also been disclosed. Chromates and manganese salts have been suggested as curing accelerators.

Properties. Hardboard is usually made in thickness of $\frac{1}{8}$ to $\frac{5}{16}$ inch. It is workable with ordinary woodworking tools but carbide tip tools are preferred for continuous use. Almost any surface finish may be applied. Sheets can be bent to single curvature. The minimum radius of bending varies with the method of bending.

Applications. Table 7.4 gives examples of applications. There is overlapping of applications of plywood, particle board, and hardboard. Economics, availability, appearance, ease of application, physical properties, and probably other factors enter into the selection.

TABLE 7.4. HARDBOARD USES

<i>Housing</i>
Interior paneling
Floor surfacing
Exterior siding
<i>Millwork</i>
Insert panels in doors
Surface panels for flush doors
Paneling for railroad cars
Prefinished wall panels for kitchens and bathrooms with dry wall construction
<i>Furniture</i>
Parts for cabinets
Bottoms for drawers
Paneling for furniture
<i>Miscellaneous</i>
Facing material for reusable concrete forms
Facings for plywood
Templates and assembly jigs
Advertising displays
Dies for forming metal (special densified hardboard)
Base and panels for electrical equipment (densified)

MOLDED WOOD WASTE

This material is essentially a molded and cured mixture of wood particles and 10 to 20% of resin plus small amounts of stearates or wax for mold release and water resistance.

Molded wood waste has tremendous possibilities. Where it is applicable, it frequently brings about savings in raw material cost, increased production rates, and the elimination of some operations as compared to other production methods.

In 1957, Midyette⁹ gave the cost of an average wood waste mix molded to a specific gravity of 1.0 as \$3 to 4 per cubic foot or approximately that of kiln-dried birch lumber. He considered a low cost for plastic materials exclusive of expanded or foamed products to be \$10 per cubic foot.

Comparisons of costs of an article made from solid wood and molded wood waste depend mainly on the labor cost of production by the two methods. One cost advantage of molded wood waste is the absence of waste from the molding operation. In general, all of the wood waste mix charged to the mold comes out as finished product.

Various kinds of wood waste may be used although they do not all give the same results. Softwoods make stronger molded articles but the hardwoods give better water resistance. The wood is ground in a manner to preserve fibers as much as possible.

Resins Used. Phenolic resins are used where high strength and water resistance are essential. Their fast cure and rapid flow are useful characteristics. Both resoles and novolaks are used. Usually, several varieties of resin are offered to meet various application conditions. Typical resins for this use have properties in the following ranges:

Capillary melting point, °C.	70–85
Set time at 150°C., sec.	15–110
Glass plate flow, mm	5–35
Sieve test, through 200 mesh, %	95–98

Molding. The molds are usually of the positive type in which the mold closes against metal lands. The wood

particle-resin mixture is capable of very little flow in the mold. Thin sections and abrupt changes in cross section are avoided in the design of the molded article. Best results are obtained when the article is reasonably flat.

Pressures of 500 to 1200 psi are commonly used, with mold temperatures of 300 to 350°F. Molding time varies with the mold temperature, the thickness of the molded part, the character and proportion of resin, and the moisture content of the charge.

Processing of Molded Parts. Drilling, turning, sawing, or other operations are not greatly different from those used on normal wood except that the presence of the resin makes them a little more difficult. Carbide-tipped tools are needed for continuous operation. In order to get adequate adhesion of surface coatings, it is generally necessary to apply a special primer.

Properties of Molded Parts. Molded parts show the following differences when compared to solid wood:

Surface	Harder and more impervious to liquids. Less resistant to wear (uncoated).
Resistance to water	Absorption rate 10–50% of that of dried wood. On penetration, moisture affects physical properties more severely.
Dimensional stability	Better than radial or tangential grain wood but frequently not as good lengthwise of the grain.
Density	Up to 50% greater than the common woods.
Flexural strength	Superior to wood across the grain and inferior to wood with the grain. Comminuting the wood and reforming averages the strength in the several directions.

Applications. According to Midyette,⁹ about 8½ million lb of resin were used in the United States in 1955 for

TABLE 7.5. PRESENT AND POTENTIAL APPLICATIONS OF MOLDED WOOD

<i>Accessories</i>	
Bathroom cabinets	Brush backs
Buttons	Heels for women's shoes
Hamper tops	Toilet seats
<i>Appliances</i>	
Bases	Handles
<i>Furniture</i>	
Chair arms and seats	Decorative pieces
Legs	Stool tops
<i>Housewares</i>	
Bowls	Lazy susans
Trays	
<i>Industrial</i>	
Coasters	Supports
Skids	
<i>Sports Equipment</i>	
Bowling balls	Bowling pins
Croquet balls	Shuffleboard disks
<i>Toys</i>	

molding wood waste. He estimated that about 6 million lb of that were used in toilet seats. Numerous other applications have been suggested and many of them offer good potential for growth. Table 7.5 lists a number of present and potential applications.

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8. BONDING AND IMPREGNATING AGENTS

ABRASIVES

The abrasive products considered here are grinding wheels and abrasive-coated disks, sheets, and belts. The basic components of these abrasive tools are suitable abrasive grains and a binder to hold them. Occasionally, fillers and reinforcements are added.

Resins

Synthetic resin binders have been widely adopted. They permit better uniformity and control of abrasive products than the older types. Through their use it has been possible to raise the peripheral speed of abrasive wheels and get faster and better grinding.

Phenol-formaldehyde resins are used in the great majority of cases. Consumption of phenolic resins in abrasive wheels

and coated abrasives in recent years, as reported by the U.S. Tariff Commission, was as follows:

1957	16.8 million pounds
1956	15.1 " "
1955	15.8 " "
1954	10.1 " "

Probably a little more than half of the resin is used in coated abrasive products.

Abrasive Wheels

Controlled variation of abrasive, binder, and pore space regulates grinding characteristics of the wheel. They are made for very rough grinding (snagging) and for mirror finish grinding. Performance of today's grinding wheels is far ahead of performance of a relatively short time ago.

Abrasive Grains. Corundum and diamonds are the two most effective naturally occurring abrasive grains. They have been supplanted to a great extent by synthetic abrasives which have more uniform grain size and structure.

Hardness of an abrasive is not the sole criterion for judging it. Chemical reactions play a very definite role in the grinding process.¹ Some very hard materials have been found to react so fast at grinding temperatures that they were useless for grinding.

Binders. Binders are usually made up of two parts: a liquid which is used to wet the surface of the abrasive grains and a powdered resin which is anchored to the abrasive grains by the liquid film until the mass can be pressed and heat cured. During the curing process, the liquid and powdered resins merge into one binder.

Alkali-catalyzed phenolic resins are used extensively as

the wetting agent, even though they have a limited storage life and could be more uniform in composition. The amount varies with the materials and conditions. As little as 5% of the powdered resin will frequently suffice. Quality of the binder is judged best by preparing and testing bars of abrasive.

Powdered Resin. The powdered resin is commonly a two-stage phenolic. Phenol-formaldehyde condensates prepared with ammonia or amine catalysts and acid-cured phenolics have been disclosed in patents. Alloys of phenolics with epoxy resins, polyvinyl butyral, and synthetic rubbers are coming into use. Some of these alloys show superior strength, flexibility, and heat resistance.

The amount of powdered resin used is adjusted to the materials used and the type of wheel to be made. Usually it is in the range of 5 to 9%. Properties of the straight phenolic resins generally lie within the following ranges:

Capillary melting point	65–95°C.
Glass plate flow	Nil to 55 mm
Cure at 150°C.	45–95 sec.

Standardization of particle size of the powdered resin is important. Many grades will pass 99% or better through 270 mesh screen.

Processing. The basic process of making grinding wheels consists of the following steps: (*a*) thoroughly coating the abrasive grains with the wetting agent; (*b*) mixing the powdered resin with fillers, if any, and blending the mixture with the coated grains; (*c*) molding cold at 2000 to 4000 psi to densities that may range from 0.064 lb/cu. in. for soft wheels to 0.110 lb/cu. in. for very hard wheels; (*d*) removing the shaped mass from the mold and baking. A stepwise time-temperature schedule is carefully followed

during the baking. Top temperature is usually about 375°F. The schedule is adjusted to the hardness desired in the product and the thickness of the parts. Cooling is also scheduled carefully to avoid setting up stresses in the wheel. The curing process may require 24 to 56 hours plus cooling.

Process for diamond wheels differs in that a rim of diamond-bearing composition is bonded to a molded phenolic disk.

Properties

The great number of compositions in use for abrasives naturally creates considerable variation in properties of the products. Test bars of an average phenolic bonded abrasive show flexural strengths at room temperature of 3500 to 5000 psi. Tensile strengths usually run about 40% lower. With proper formulation, tests at about 350°F. will show a drop in strength of only a few per cent. Alloying the phenolic with an epoxy resin improves strength.²

COATED ABRASIVES

This term is applied to disks, sheets, and belts, to the surface of which abrasive grains have been bonded. Coated abrasives are rapidly coming into use, taking the place of abrasive wheels in some instances. Improvements in coated abrasives and developments in operating methods and equipment for using abrasives have contributed to this.

Backings for coated abrasives are paper, fabric, vulcanized fiber, and their combinations. The abrasive is generally flint, silicon carbide, or aluminum oxide.

Production

Coated abrasives are generally produced as a continuous operation composed of the following steps:

1. Roller application of a film of resin to the backing.
2. Application of abrasive grains to the wet resin film by sprinkling, electrostatic attraction, etc.
3. Precuring of the resin at low temperature (120 to 130°F.).
4. Roller application of a top coat of resin.
5. Oven-curing of the resin.

The time and temperature for oven-curing vary with the type of oven and the rate of travel of the material. An example is a 4-hr cure at 140 to 200°F. With some equipment, temperatures of 200 to 250°F. are used. For greater toughness the abrasive sheet is postcured at 250 to 275°F.

Binders

About half of the coated abrasives are made with phenolic resins. Animal glue and urea resins share the rest. Phenolic resin-bonded coated abrasives can withstand more strenuous wear than the others. They can be used with soluble oil and water coolants.

Phenolic resins used in coated abrasives are the alkali-catalyzed, hydrophilic type. They are available in several viscosity ranges and usually have solids contents of 65 to 75%. Like other resins, they are unstable at normal room temperatures.

More uniform and more stable resins with better adhesive ability and water resistance are needed. Development work is active. One method of improving water resistance of coated abrasives is to coat the abrasive grains with a

thermosetting vinyl polysiloxane before bonding with a phenolic resin.³

FRictional Materials

Brake linings and clutch facings are the principal items in this group. Resin consumption for clutch facings has declined somewhat with the wider adoption of automatic transmissions in automobiles.

Several types of linings are recognized. In one type, a fabric of asbestos fiber, cotton fiber, and wire is impregnated with resin and compressed or laminated under heat. In another type, an asbestos fiber-liquid resin composition is extruded. The extruded material is next dried and partially cured. It is then compressed by calendering or pressing and baked to complete the cure.

Much brake-lining material is produced by mixing powdered resin with asbestos fibers, plus other fillers and/or additives. Resin content is usually 15 to 30% by weight, depending upon the amount and specific gravity of the filler and other additives. For thin linings, the composition is press-molded in sheets and partially cured. The sheet is then cut as desired, and the segments are shaped and given a final cure at 300 to 400°F.

Thicker linings are molded to shape. After curing at 300 to 400°F. they are usually baked at about 350 to 400°F. to increase their temperature resistance. Baking is frequently carried out according to a schedule of increasing temperature.

Binders

For good heat resistance, resistance to oil and water, and wearing qualities, linings made with phenolic-resin binders

are outstanding. It is estimated that about 70% of friction materials are bonded with phenolic resins. The U.S. Tariff Commission reported consumption of 15 million lb of phenolic resins in frictional materials in 1957 and 25 million lb in 1955.

Phenolic resins for frictional elements are commonly of the two-stage type. Their melting points are usually in the range of 55 to 105°C., and their cure time at 150°C. ranges from 40 to about 350 seconds. Both the formaldehyde and the furfural types of condensates are used. In some instances it has been thought that the furfural-type condensates gave a more even cure. Straight phenolics are used but are exceeded in volume by oil-modified phenolics. Oils used for modifying the phenolics are linseed, tung, castor, and cashew nutshell. Some of the phenolic alloys are finding use here and should become more popular.

Mounting of Linings

Brake linings were formerly riveted to the brake shoes. It has been demonstrated that adhesive bonding is more satisfactory from all angles. Tape can also be used in the bonding of the lining to the brake shoe. Tilden⁴ soaks an asbestos fiber sheet in an alcohol solution of a phenol-aldehyde condensate and a small proportion of isophorone. The sheet is dried to remove the alcohol. During the heat and pressure bonding of the tape between the lining and the shoe, the isophorone aids flow of the resin and is then evaporated. The isophorone also increases the shelf life of the tape.

INSULATION

Large quantities of glass fiber and rock wool are bonded into batts and blankets for heat insulations. The density is

usually about 2 to 3 lb/cu. ft. Coefficient of thermal conductivity is close to the lowest of the usual insulating materials.

These products are used for the insulation of buildings, transport vehicles, refrigerators, ovens, and the like.

Resins

Because of their durability, water resistance, and heat resistance, phenolic resins hold an almost exclusive position as the binder. According to the U.S. Tariff Commission, over 50 million lb of phenolic resins were used for this purpose in each of the years 1955–57.

The amount of resin used changes with the density desired in the finished batt or blanket and with the degree of stiffness needed. Rock-wool batts of average density require approximately 2 to 3% of resin by weight of the fibers. Glass fibers require about 50% more resin than rock wool. Theoretically the resin should be applied only where the fibers cross each other. The viscosity and solids content of the resin and the method of application are selected with the intent of approaching this as nearly as possible. Resin supplied to a given user requires particular attention to lot-to-lot uniformity.

Liquid Resins. The liquid phenolics are water-soluble types and are available in a number of varieties. A composite of their properties as produced is shown in Table 8.1.

TABLE 8.1. LIQUID PHENOLIC RESINS

Viscosity at 25°C.	30–650 cps
Nonvolatile content	50–70%
pH	6.5–8.5
Alkalinity as Na ₂ O	0.08–0.20%
Water miscibility	800% to infinity

For application, the resin is generally diluted with water and ammonia to a nonvolatile content of 10 to 16%. Frequently "Vinsol" emulsion (a product of Hercules Powder Company) is added to the diluted phenolic resin. About one-third as much emulsion as phenolic resin is the usual ratio.

The instability of the liquid phenolics makes it necessary to chill the material for shipment and keep it in cool storage. Considerable attention has been given to the use of powdered resin.

Powdered Resin. The powdered resins used here are finely divided single-stage resins with relatively low melting points of 55 to 65°C. Glass-plate flow is usually about 25 to 45 mm. In preparing blankets or batts, the fibers are separated by carding or combing and blown into a mixing chamber together with the powdered resin. A blanket is formed and cured in essentially the same manner as with liquid resins.

The solid-resin process is applied to glass fibers and to some extent to cotton, nylon, and other organic fibers. The product goes into automobile insulation, rug pads, furniture padding, and the like.

Processing

In preparing insulation, rock wool or other inorganic fibers are blown into a mixing chamber. Simultaneously a diluted phenolic resin is sprayed into the chamber where the resin deposits on the fibers. Fibers and resin are carried out of the chamber on a traveling belt and through a curing oven at 350 to 550°F. There water is evaporated and the resin is cured. At the same time the fibrous mass is compressed by a superimposed traveling belt. After the resin is cured, the wool is cut into the desired size.

ELECTRICAL PARTS

The production of parts for electrical equipment from phenolic-molding compounds and laminates was considered in Chapters 4 and 6. Some additional applications of phenolic resins which may suggest further uses for them in this field are reviewed briefly below.

Anodes: Thrune⁵ bonds graphite with a phenolic resin and a phosphate modifying agent.

Battery Separators: Many disclosures have been made of materials and methods for the preparation of separators for storage batteries to replace the wood sheets previously used. Apparently several million lb of resin a year are used, and the volume is growing.

The simplest process is the impregnation of cellulose sheets which are dried and cured.^{6,7} Phillips⁸ combines two sheets of glass fibers. One is bonded with phenol-formaldehyde resin. The other is coated with an emulsion of butadiene-styrene copolymer. Merrill⁹ impregnates a pulp of glass and cellulose fibers and forms a separator with reinforcing ribs.

Magnet Cores: Metal laminates for magnet cores are bonded with a mixture of resorcinol-formaldehyde resin and a vinyl resin. The adhesives are temperature-resistant and do not cause tensions which could change the magnetic properties.¹⁰

High-frequency magnetic cores are prepared from reaction products of Co_2O_3 , and Fe_2O_3 . The composition is bonded with phenol-formaldehyde.¹¹

FOUNDRIY CORES AND MOLDS

There are two principal uses for synthetic resins in foundries: binders for sand cores and binders for shell

molds. Separate varieties of resins are used for each. Annual consumption of synthetic resins in foundries is approximately 16 to 20 million pounds.

Foundry Cores

Thermosetting synthetic resins came into use as binders for foundry cores during World War II. Oils, natural resins, and cereals were the type of materials used up until then. A typical synthetic resin composition for cores is the following example. In this and other formulas control of water content is very important.¹²

Material	Parts by Weight
Sand	100.0
Cereal	1.5
Synthetic resin	0.75
Water	3.0
Kerosene	0.5
Parting agent	0.05

The ingredients are thoroughly blended, formed into the shape of the core, dried, and baked to cure the resin. A good core must have adequate strength before curing, high strength after baking, sufficient heat resistance to receive and hold hot metal until it sets, and yet burn out at the proper time for collapse of the core. Each of the components of the above formula has a definite use.

Advantages. Cores made with synthetic-resin binders are generally superior in some respects to those made with oils or natural resins. Some of the advantages are: better core properties, especially strength and heat resistance; smoother surfaces on castings; reduced baking time and more effective use of equipment; reduced costs; less fumes to gum up equipment and pollute foundry room air; and better collapsibility of cores.

Resins. Water-soluble resins are commonly used. They

are preferably of a type that is reduced to a thin consistency by relatively little water. This aids in wetting of the sand by the resin. As the core is dried out and baked, the resin cures to the infusible and insoluble stage and binds the sand. Phenolic and urea resins are each used. The annual consumption of resin is approximately 3 to 4 million pounds. The phenolic resins are of the alkali-catalyzed type and are supplied by producers in several varieties to meet various operating conditions. Being single-stage resins, they gradually react in storage at room temperature and above and should be stored cool.

Phenolic resins have a higher heat resistance than the ureas and are therefore commonly used when steel, gray and malleable iron, brass and bronze are to be cast. The phenolic resin is usually in the range of 0.5 to 1.5% on the weight of the sand.

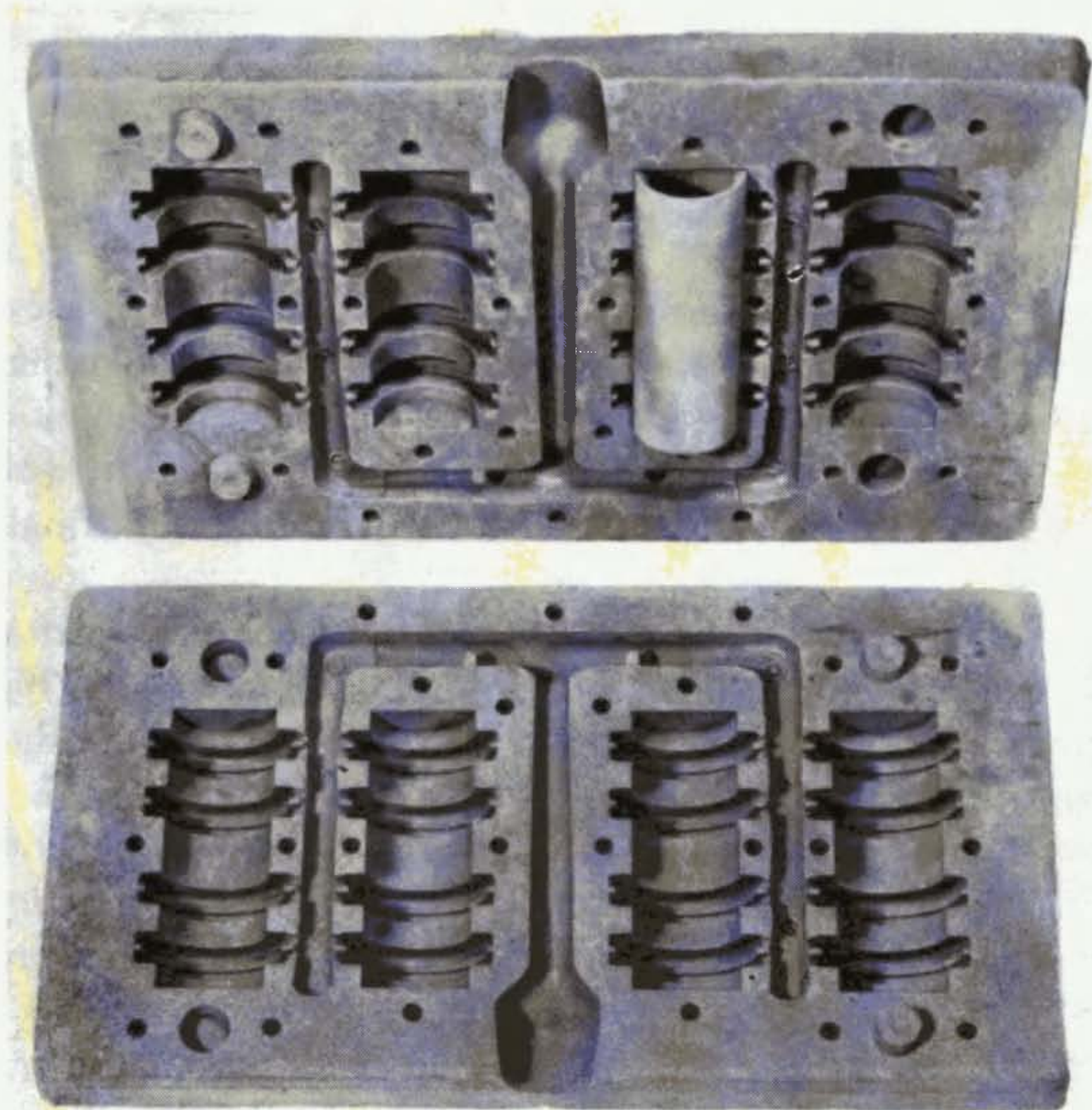
Core Treatment. Before a core is used in a mold, the surface is usually treated with a coating to improve casting quality. Salzberg and Kinney¹³ have shown that aqueous solutions of phenolic resins sprayed onto the surface of the cores improve the strength and the surface quality.

Shell Molds

Foundry molds are made in increasing amount by the "shell mold" process, also known as the "Cronin" process or "C" process. Such molds are made of matched pairs of shells composed of sand and a low proportion of resin. They are fairly porous and relatively thin, e.g., $\frac{1}{8}$ to $\frac{3}{8}$ in. thick.

Advantages. Shell molds are in use in a wide variety of foundries.¹⁴ Automotive and machinery manufacturers have found them very useful. The process is not applicable to every type and size of casting. Nevertheless, they have been used for casting most of the metals normally cast. The size

of castings has ranged from less than an ounce up to several hundred pounds. Molds for small articles generally have multiple cavities, as shown in Figure 8.1.



(Courtesy The Borden Chemical Co., a Division of The Borden Co.)

Figure 8.1. Multiple unit shell mold: size of mold, approximately 9½ x 17 inches.

Where it is applicable the process has demonstrated definite advantages, such as:

1. Excellent surface finish on castings.
2. Close dimensional tolerance in castings.
3. Greater detail in castings.

4. Permeability of the shell permits molding of thinner sections.
5. Consistent pattern reproduction.
6. Production is adaptable to automatic operation.
7. There is less scrap metal, more good castings per ton.
8. Less sand and resin are required.
9. Molded parts require less machining.
10. Unskilled labor can be used.
11. Production can be increased and space decreased.

Operations. The shells are made by contacting a hot pattern with a sand-resin mixture. The resin near the pattern fuses and binds the sand. When a sufficient thickness of bonded material is built up, any excess sand-resin is removed and the shell is baked to cure the resin and make a rigid shell.

Originally, shells were made using a mechanical mixture of novolak resin, hexamethylenetetramine, and sand. Difficulty in maintaining uniformity of composition of the shell has led to increased use of resin coated sand. The best results are generally obtained by applying the resin as a solution in an organic solvent. The method has practical difficulties and various other methods have been proposed.^{16, 17, 18}

In applying the sand-resin to the hot pattern, the mix may be dropped onto the pattern. After a sufficient time the pattern is inverted to remove free sand-resin. This is generally known as the “dump-box” method. Much of the operation is now handled automatically. A recent survey indicated that about 85% of the foundries making shell molds use this method.

According to a more recent method, the sand-resin is blown into a boxlike structure, one wall of which is the hot pattern. This is the “blowing” method. Shells so formed are processed as in the other method.

Casting. To make the mold, matched shells are clamped or cemented together. Gates and risers are already formed in the shell. For heavy castings the mold is supported to prevent distortion by the hot metal. One method of doing this is to surround the mold with metal shot. The material of the mold generally burns out sufficiently to make removal of the mold an easy task. In some cases sand in the mold is recovered for reuse.

Materials. The sand is selected for degree of fineness, particle size distribution, grain structure, and freedom from impurities.

Phenolic resins have been used predominantly, although numerous other types have been proposed. The proportion varies from 2 to 6% of the sand with an average of about 4%. The phenolic resin is usually a novolak and is commonly grindably hard. The characteristics of the resin vary with the formulation ideas of the producer and the specifications of the foundry. Smith¹⁵ has described an ammonia-catalyzed phenol-formaldehyde resin. It is claimed to be particularly suited for shell molds in that it is free from blowing tendencies, is low in alkali metal content, and has good flow properties. Typical properties of shell molding resins are shown in Table 8.2.

TABLE 8.2. POWDERED SHELL MOLDING RESINS

Capillary melting point	85–95°C.
Cure time at 150°C.	65–96 sec.
Glass plate flow at 125°C.	18–38 mm
Sieve test—through 100 mesh	100%
through 200 mesh	80%

Occasionally a liquid novolak is used, and there are indications that liquid resins may grow in popularity. Fitko and Horn¹⁶ describe the production of one type using less

formaldehyde and lower temperatures than usual for condensation with novolaks.

PAPER

There has been considerable interest during the past few years in the beater addition of phenolic resins in the production of paper for oil filters, overlay sheets, laminate plies, and other applications. A successful process would have an economic advantage over the present process of dry-saturation of paper. The most promising developments appear to be the use of combinations of phenolic resins and synthetic rubbers and the use of precipitating agents other than alum.

Data from tests on paper formed with phenolic resin and nitrile rubber are given in Table 8.3. The product is recommended for shoe inner soles, box stock, tubing, building boards, and flooring felts.

TABLE 8.3. CELLULOSE-RESIN SHEETS^a

	No Resin	Rubber Latex ^b	Phenolic Resin ^c	Phenolic Plus Latex
Dry tensile, psi	30.8	37.6	60.0	66.5
Wet tensile, psi	8.5	17.6	31.2	37.6
Dry burst (Mullen)	45.8	65.0	79.8	88.7
Relative stiffness	1.00	0.93	1.27	1.86

^a Data from U.S. Patent 2,785,975. Cure—250°F. for 24 hours.

^b Using 15% of butadiene-acrylonitrile latex.

^c Using 15% of phenol-formaldehyde dispersion at pH 12.3, carried to incipient C stage.

Impregnation

Frequently for one of several reasons it is desired to treat paper with a phenolic resin. Normally the treated sheet is

undesirably brittle. By using nitrile rubber in combination with a compatible soluble phenolic resin, a satisfactory impregnating material is obtained. A small amount of ammonium caseinate is used to stabilize the system. Table 8.4 gives some results obtained with a series of such blends.

TABLE 8.4. PHENOLIC RESIN-NITRILE RUBBER IN SATURATED PAPERS

Phenolic resin/Hycar* 1562 ratio	1/1	4/3	2/1	4/1	1/0
Ultimate tensile strength (lb/in. width, dry)	17.1	17.1	16.0	19.0	12.0
Ultimate elongation (% , dry)	6	6.5	5	4.5	2.5
MIT Fold (cycles, dry)	55	44	33	26	18
Cured 5 minutes at 120°C.					
Ultimate tensile strength (lb/in. width, dry)	17.6	18.4	19.9	23.9	23.4
Ultimate elongation (% , dry)	5	3	2.5	2.5	2.5
MIT Fold (cycles, dry)	54	23	7	2	11
Cured 10 minutes at 120°C.					
Ultimate tensile strength (lb/in. width, dry)	17.5	16.0	18.2	19.0	21.0
Ultimate elongation (% , dry)	5	5	4	3.7	3.0
MIT Fold (cycles, dry)	67	33	22	16	25

* Registered trade mark of the B.F. Goodrich Chemical Company. Data courtesy of the same company.

Pigment

Leek¹⁹ has proposed to prepare a pigment for paper-filling or coating by spray-drying a mixture of clay and a water-dispersed phenol-formaldehyde resin. The powder is mixed with water and starch or other adhesive for coating paper.

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9. COATINGS

Some of the earliest phenolic resins were developed as shellac substitutes. The use of phenolic resins in varnishes was introduced nearly forty years ago.

Phenolic resins are still used rather extensively in protective coatings. The patent literature indicates continued interest in their development. Collectively, their properties are excellent, they are easy to apply, and their cost is relatively low. Coatings prepared from them excel in the following properties:

Heat and fire resistance
Dielectric strength
Durability
Abrasion resistance

Hardness
Chemical resistance
Mechanical strength
Water resistance

In spite of these favorable features, the consumption of phenolic resins in protective coatings has remained essentially constant during the past seven years. This is shown in Table 9.1. The annual average of actual phenol-formaldehyde resin is estimated to be about 32 million lb. The rest is mainly rosin.

Color and the cure required have held phenolics back in this field. From the standpoint of color, 100% phenolics lack aesthetic appeal. The films from many of them tend to

yellow on exposure, but progress is being made toward correcting it.

TABLE 9.1. PHENOLIC RESINS IN PROTECTIVE COATINGS

(millions of lb)	
1951	54
1952	43
1953	50
1954	43
1955	52
1956	51
1957	54

Baking adds to the hardness and durability of certain phenolic coatings but it is not always practical to bake an article in order to cure the resin. In such cases, phenolics frequently lose out to other types of coatings.

TYPES OF COATINGS

Surface coatings that provide the major outlets for phenolic resins are oleoresinous and spirit varnishes. Lacquers provide no significant outlet. Interest has been shown in the use of lowly condensed phenolics in polyvinyl acetate lacquers.

Oleoresinous varnishes are compositions of resins and drying oils which are heat treated and then diluted to workable consistency with volatile solvents. The varnish dries by evaporation of the solvent and oxidation of the residue. Properties of the films vary with raw materials, processing, and presence or absence of modifiers.

Spirit varnishes are solutions of resins or resin-drying oil compositions, generally in alcohol or alcohol-hydrocarbon.

After the solvent has evaporated, the film is usually baked to get full hardness and durability.

PHENOLIC MATERIALS

Four main groups of phenolic materials are used in coatings: (*a*) 100% phenolics—soluble in drying oils; (*b*) modified phenolics—made soluble in drying oils by reaction with rosin or other materials; (*c*) baking resins—used in alcohol solution and baked after evaporation of the solvent; (*d*) dispersion resins—polymerized phenolic-drying oil dispersed in aromatic hydrocarbon. Combinations of phenolics with other resins have also been suggested.

100% Phenolics

Both acid and alkali-catalyzed resins are used. Best oil solubility is obtained by the use of *ortho* or *para*-substituted phenols. Alkyl substituents are preferred to aryl. Color stability is best when *para*-substituted phenols are used. Principal phenols are *para-tert*-butyl phenol, *para-tert*-amyl phenol, *para*-phenylphenol, and *para*-cyclohexylphenol.

To improve resistance to alkali and color stability of the varnish films, Bender and Farnham¹ condense phenol and certain homologues with formaldehyde and then esterify most of the aryl-hydroxy groups in the resin chain. The films are acid-hardened.

Alkali-Catalyzed Resins. These range from liquids to solids of softening points of 215°F. They are mildly reactive with drying oils and build up the viscosity of the varnish. When Chinawood oil or Oiticia oil is used the varnish dries rapidly. Films show water and alkali-resistance and have pronounced elasticity.

A few illustrative uses for the varnishes are:

Marine spar varnish	Chemical resistant coatings
Floor and deck enamels	Food container linings
Insulating varnish	Heat sealing compounds
Shade cloth finishes	Swimming pool finishes

Acid-Catalyzed Resins. They are usually solid resins softening in the range of 85 to 140°C. There is very little reaction when they are cooked with drying oils. The varnishes are pale and have good color stability. Films are resistant and have pronounced elasticity.

Typical uses are:

Alkali-resistant finishes	Cold cuts added to alkyds, lacquers, and spirit varnish to improve water resistance.
Anti-corrosive primer	
Oilcloth finishes	High durability finishes for boats, bridges, freight cars.

Miscellaneous Resins. Several condensation products of phenols with terpenic materials have been described. Norton and Less² react a phenol with terpineol or related materials in the presence of an acid catalyst. The resins have an unusual lightness of color, a low acid number, and a high melting point. They are oil-soluble and oil-reactive. The varnishes tolerate mineral spirits thinner.

Swallen³ condenses phenol first with butyraldehyde and then with formaldehyde under acid conditions. Kleinicke⁴ condenses *para*-cumenylphenol with formaldehyde in the presence of trichloroacetic acid and obtains a light colored resin with a melting point of 80°C. It is completely compatible with linseed oil. Turner and associates⁵ condense phenol and an aldehyde under acid conditions. The condensate is then heated with free monohydric phenol or a styrene in the presence of a Friedel-Crafts catalyst. The product is oil-soluble.

Modified Phenolics

These resins exceed 100% phenolics in volume of use in coatings. Rosin is the principal modifying agent. U.S. Tariff Commission data are given in Table 9.2.

TABLE 9.2. ROSIN-MODIFIED PHENOLIC RESINS, 1957

	Production (Million lb)	Unit Value \$/lb
From phenol-formaldehyde	23	0.26
From <i>p-tert</i> -butyl phenol	4	0.26
From bisphenol	4	0.25
Total	31	

Rosin-modified phenolics have an important combination of solubility, viscosity, and drying characteristics and the films have hardness and water resistance. Because of the low proportion of phenolic resin these resins are sometimes erroneously considered to be merely rosin extensions of phenolics. It has been demonstrated that they are more than that.⁶

The phenolic resins used here are commonly of the alkali-catalyzed type and are rather lowly condensed. Acid-catalyzed resins serve occasionally in special applications.

Resin Preparation. Rosin (60 to 90 parts) and phenolic resin (10 to 40 parts) are heated rather gently to solution. The resin is then esterified with glycerol, pentaerythritol, or other polyhydric alcohol to the desired acid value, for subsequent reaction with the drying oil.

Frequently, the resins are matured before being cooked with the oil. One method is by vacuum heat treatment for 12 to 24 hours. This builds up the molecular structure and improves chemical resistance, solubility, and physical properties.

Varnish Preparation. The resins dissolve readily in the oil and the cooking procedure is very simple. Top temperature is usually lower than when 100% phenolics are used. The varnishes have good bodying property.

Uses. The following list shows some of the many applications for these varnishes. Varnishes made from bisphenol resins are particularly well suited for use in enamels unless the lightest colors are required.

Aluminum vehicles	Household enamels
Artificial leather coatings	Machinery finishes
Floor enamels	Transport vehicle finishes
Foul weather fabrics	Trim paints
Grinding vehicles	

Baking Resins

These coatings are applied as resin solutions or spirit varnishes. Baked films are superior in hardness, resistance to solvents and chemicals, low-permeability to water vapor, abrasion, and adhesion. An exception to good adhesion to metals occurs with highly polished steel.

Films withstand exposure to temperatures up to 700°F. for short periods. When flexibility of film is needed, as in coatings for sheet metal that is to be formed after coating, the resin may be plasticized with other resins.

Alkali-catalyzed phenol-formaldehyde condensates are used in the majority of cases. Blocked phenolics, in which the hydroxyl groups have been reacted with some reagent, are being used in increasing amounts. They have the good properties of ordinary phenolics plus improved resistance to alkalies and oxidizing agents. They are also more compatible with other resins.

The resin may be soluble in alcohol or it may require an alcohol-aromatic hydrocarbon mixture or a "Cellosolve" type solvent. Proposals have been made to use water solu-

tions but the performance has apparently not come up to expectations. They are not now active.

Dispersion Resins

Dispersion resins are prepared by heat processing phenolic resins with drying oils and a dispersing agent. The oils are gelled by the treatment but remain in a dispersed condition. Aromatic solvents are used as thinners.

In general, phenolic resins for this type of coating are similar to those used in rosin-modified phenolics. The drying oils are selected according to whether a hard gel or a soft gel is desired.

Properties. The films are nonoxidizing and dry by evaporation of solvent. Drying is rapid and in many cases the film may be sanded after one-half hour. Films have excellent adhesion and good weather resistance. They lack the gloss of films from oleoresinous and spirit varnishes. In other properties they are a little inferior to the varnishes.

Uses. The quick-drying nature of these materials and their adhesiveness make them of value in primers over metal, in shop coats, and in traffic paints. They are not affected materially by lacquer solvents and serve well as lacquer undercoats.

Another use of these resins is blending with alkyd resins or varnishes to reduce drying time and increase resistance to chemicals.

Combinations With Other Resins

Numerous combinations have been suggested. Some resins form alloys with phenolics, some react with phenolics, and some function essentially as fillers. A phenolic pigmented with tetrafluoroethylene gives films which have the desirable surface characteristics of the tetrafluoroethylene.

German Patent 956,987 discloses the preparation of acid-resistant coatings from phenolic resins containing as filler an acrylic resin, polyvinyl chloride, polystyrene, or other resin in powdered form.

Some of the more important combinations of resins that are cured together are considered in the following paragraphs.

Alkyd Resins. Phenolic resins are frequently added to alkyds during the processing of the latter. Films are tough, durable, fast-drying, and moisture resistant. They adhere well to metals and make good insulation varnish. The combination is useful in interior colored finish where resistance to soap is required.

Epoxy Resins. Phenolic resins function as curing agents for epoxy resins. Combinations of unmodified phenolic resins and epoxy resins are finding increasing use in coatings where resistance to chemicals, oils, solvents, and abrasion is of top importance and color is secondary.

Usually the two resins are combined in solution. The phenolic component is 25 to 60% of the total resin, according to the properties desired. A small amount of a flow control agent and a catalyst, such as phosphoric acid, are added.⁷ Films are dried and baked.

So-called precondensed resins are made by reacting epoxy resin with a limited amount of phenolic resin. Subsequently, any of several types of curing agents is added and the condensation is completed during the curing of the film. Butylated phenol-formaldehyde resin is said to be well suited to this process.

Organosilicon Compounds. Coating compositions have been prepared from the reaction product of phenyl methyl siloxane or diphenyl siloxane, glycerine, and linseed oil and oil-soluble phenol-formaldehyde resin. Films are reported to have good durability, weathering, and gloss retention.

Polyamide Resins. Baking finishes have been prepared

from reactive combinations of highly branched liquid polyamide resins and heat reactive phenolic resins.⁸ A wide variety of phenolic resins may be used. The main requirement is that they have reactive methylal groups. Solutions in toluol-isopropanol have good storage life. Baked films have an excellent combination of toughness and chemical resistance.

Polyvinyl Resins. Polyvinyl formal and polyvinylbutyral resins have been used for a long time in combination with phenolic resins as wire enamels. The baked films are hard, tough, flexible, and abrasion resistant.

Barr⁹ disclosed a coating for metal containers composed of vinyl chloride-vinyl acetate copolymer and phenolic resin in a volatile solvent. When the solvent evaporates, the phenolic resin is said to migrate to the metal surface and improve the adhesion and thermal stability of the coating.

Urea Resins. Combinations of alcohol-soluble phenolic resins and urea-formaldehyde resins yield films with superior hardness, flexibility, adhesion, and resistance to acids, alkalies, and solvents. Proportion best for many uses is 70 parts urea resin and 30 parts phenolic resin.¹⁰

It has been reported that better results are obtained if a phenol-urea mixture is condensed with formaldehyde. Baked films are said to show no discoloration and to be resistant to boiling water, organic solvents, and dilute caustic.¹¹

Special Coating Materials

A few examples are given below to illustrate novel applications or to emphasize the versatility that is possible in a given type of application.

Antisweat Coating. A mixture of phenolic-drying oil varnish, diatomite, and a small amount of fibrous material is applied as an aqueous emulsion.¹²

Coating for Food Products. Perishable agricultural products are contacted with an extremely dilute solution of a salt of *ortho*-phenylphenol and hexamethylenetetramine.¹³

Fire-Retardant Coatings. Phenolic resins of themselves offer a certain amount of resistance. Various compositions have been proposed to improve this. Nason and co-workers¹⁴ add the reaction product of phosphorus oxychloride and ammonia. Wachter¹⁵ incorporates zinc borate in a varnish, together with a small amount of citric or other selected organic acid as stabilizer.

Metal Coatings. Phenolic baking varnishes are among the outstanding materials for this purpose. The 100% phenolictung oil varnishes give particularly good results. Pigmented coatings of that type have given years of service on canal gates. Blocked phenolics are gaining acceptance by virtue of their alkali resistance and compatibility.¹⁶ Alcohol-soluble phenolics produce films of very low permeability. Combinations of phenolic resins and vinyl resins, referred to above, are useful.

Printing Inks. In a strict sense, these are not coatings but their compositions associate them with coatings. Rosin-modified phenolics are the most important type, 100% phenolics have minor use. Bisphenol resin is the largest volume printing ink phenolic. In general, the resins have melting points between 145 and 175°C.

The phenolic resin and drying oil are merely fused together. Care is taken to avoid the formation of overpolymerized material, which encourages instability of the ink and reduced gloss of film.

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10. CASTINGS, FOAMS, AND SPHERES

CASTINGS

Commercial production of casting grade of phenolic resins in this country began thirty years ago. The 1954 Census of Manufactures reported production as nearly 6 million lb at an average value of \$0.55 per lb. Present production rate is much higher but no official data are available. Current price range is \$0.45 to 0.70 per lb.

Phenolic Resins

Phenol is the commonly preferred raw material. It is condensed with 1.5 to 3.0 moles of formaldehyde in the presence of a fixed alkali catalyst. Condensation temperature is lower than is usual for resoles. This helps to control the exothermic reaction and to maintain the desirable hydrophilic nature of the condensate. After condensation, the product is acidified, commonly with lactic acid. It is then concentrated under vacuum. For some varieties the

concentration is stopped while there is 5 to 10% of water still present. For clear resin, a small amount of glycerine or equivalent is added to act as a mutual solvent for resin and water. Condensing in the presence of polyvinyl alcohol is said to aid in the production of clear, colorless resins.

Condensates are usually thick fluid to taffy-like in consistency. Like other resoles they are thermally unstable. Many lots have been cured at 70 to 95°F. without additions but this frequently took as much as 10 days. In present practice, acidic catalysts are added to bring cure time within practical limits.

Mineral fillers or asbestos are frequently added when the resin is to be used in industrial castings. Various additives have been proposed to aid in the production of strain-free castings.¹

Casting

The resin is warmed to make it more fluid, the accelerator is mixed in thoroughly, and the mixture is poured into molds. Care is taken to prevent the introduction of air bubbles.

Practically any rigid material which will produce a smooth surface may be used for the mold. Plaster and lead are the most popular. If molds are made from casting resin they may be used several times. Cores are frequently used in large molds to save resin.

Curing

With sufficient accelerator the resin may be cured in a few minutes. In general, the dimensional control of the casting is best when the cure is extended to 24 hours or more. Castings are usually cured in controlled-temperature

ovens. The temperature may be held constant or it may be stepped up progressively, e.g., starting at 70 to 80°F., carrying further at 120°F., and finishing at 205°F. It is usually preferable to cool the mold and contents before removing the casting. Postcuring at 200°F. for a few hours after removal from the mold helps to stabilize the casting.

TABLE 10.1. CAST RESINS

	Mech. and Chemical	Asbestos- Filled	Decorative	Transparent
Specific gravity, av.	1.28	1.70	1.31	1.33
Tensile strength (1000 psi)	4-9	3-6	5-9.5	2.5-4.5
Compressive strength (1000 psi)	10-20	10-13	10-16	12-17
Flexural strength (1000 psi)	8-17	5-8	8-17	4-7
Modulus of elasticity (10 ⁵ psi)	3-7	19 av.	3-5	1-3
Impact strength, Izod (ft-lb/in. notch)	0.25-0.40	—	0.25-0.45	0.23-0.35
Resistance to heat (continuous, °F.)	—	300	160	—
Heat distortion (264 psi, °F.)	165-260	—	130-175	100-125
Water absorption (24 hours, %)	0.2-0.4	—	0.3-0.4	0.3-2.0
Dielectric strength (short time, v/mil)	350-400	—	300-450	75-250
Dielectric strength (step-by-step, v/mil)	250-300	—	200-350	40-200
Thermal expansion (per °F x 10 ⁵)	3.3-6.1	—	3.3-5.5	4.7-6.6

Properties

Cast phenolics are produced in various degrees of translucency or opacity and in colors from milk white to dark shades. In some cases, mottled or marbled effects are supplied. Industrial grades are usually yellow to grayish.

The castings are hard and rigid. They have good resistance to acids, fire, fungi, and extremes of temperature. They are weaker than the hot molded compounds of Chapter 4 both mechanically and electrically. Usual properties are shown in Table 10.1. Properties vary with formulation, condensation process and curing method.

Castings may be cut, drilled, ground, sawed, tapped, and turned with conventional tools. Parts may be buffed, lapped, or sanded. The ease of working makes the material attractive for do-it-yourself applications.

Uses

Cast phenolics are used in two distinct fields of application. In one, the beauty and decorative effect are stressed. In the other, strength and hardness are important. Table 10.2 lists some of these applications.

In the production of items in the decorative list, phenolics have suffered from competition of thermoplastics, mainly because of the easier molding of thermoplastics. In other applications, phenolics frequently compete with epoxy resins and polyesters.

Tooling. Many plants have found in plastics a means for (a) saving time and expense in the production of dies, models, and patterns, (b) for widening design possibilities, and (c) for reducing the cost of short production runs. In 1954 it was estimated that 7 million lb of plastics were used

for tooling.² Present rate of consumption is probably several times that but reliable data are not available.

TABLE 10.2. APPLICATIONS FOR CAST PHENOLICS

<i>Decorative</i>	<i>Industrial</i>
Brush backs	Check fixtures
Brush handles	Core boxes
Chessmen	Dies: Draw
Cigarette holders	Form
Costume jewelry	Pantograph
Dominoes	Stretch
Figurines	Electroplating shields
Jewel boxes	Gears
Knife handles	Jig bases
Novelties	Linings for tanks, pipe lines
Pipe stems	Master models
Poker chips	Molds: Rubber dip
Shoe heels	Vacuum forming
Statuettes	Panels and pilasters for
Toys	vending machines
Trophy bases	Foundry patterns
	Keller patterns

Cylinders, rods, sheets, slabs, and tubes for use in production of various articles

There is much difference of opinion as to materials and methods for making plastic tools. Phenolics, epoxy resins, and polyesters are used. Phenolics are used as castings. Polyesters are used as laminates and epoxy resins are used in both forms.

Low cost is usually cited as a prime advantage of phenolics. Ease of casting, low shrinkage, high temperature resistance, and good mechanical properties are other important properties. These favorable features are offset to some extent by the need for oven curing and a tendency toward brittleness.

Potentialities for plastic tooling are good but materials with better resistance to wear and heat and at lower cost are needed.

FOAMS

Developments in such industrial processes as building construction, metal forming, and insulation have increased the commercial importance of plastic foams. In 1957 it was predicted that the annual production of plastic foams would reach 300 million lb in 1960.⁴ This probably includes some foamed rubber. More recently, Goggin⁵ predicted that the use of plastic foams in the building industry will jump nearly 500% in the next several years. He also was of the opinion that urethane, phenolic, and polystyrene foams have the brightest future. Production of plastic foams in 1957 has been estimated at 29 million lb.

There are flexible and rigid plastic foams. In some instances, the same type of resin may be used for either. Plastic foams are of open or closed cell construction, i.e., the cells are interconnecting or isolated. Phenolic foams are all of the rigid type and they are usually considered as having 40 to 60% open or closed cells.

Properties and applications vary with the type of foam. Both flexible and rigid foams are commercially important. At present, flexible foams are produced in higher volume. The long range potential for rigid foams is considered to be even greater than that of the flexible type.

Homogeneous Foams

These are composed of a single type of resin within which a gas is generated by chemical action or is introduced by solution or mechanical agitation.

Phenolic foams are usually made by chemical action. Attention has been given to foaming phenolic adhesives for plywood by whipping air into them as a means of reducing glue line cost. Recent work shows some promise.⁶

Most of the important thermosetting and thermoplastic resins are used to make plastic foams. The phenolic resins used are essentially the same as those used for casting. A typical resin has a viscosity of about 25 poises at 25°C. Combinations of phenolic resin with acrylonitrile copolymers and other materials have been disclosed.⁷

Foaming agents include metals which react with acid and liberate hydrogen, nitrates or azo-compounds which evolve nitrogen, sulfonylhydrazides, and diazonium salts.

Compounding. The phenolic resin is commonly compounded with an accelerator and a foaming agent. Frequently small amounts of a surface active agent and a solvent are added to give a finer and better grain to the foam. The dosage of foaming agent is regulated according to the density desired in the foam.

The following composition used to fill a void on a Navy vessel illustrates the general type of formulation.⁸

Resin	100.0 lb
Sodium bicarbonate	0.7 "
Wetting agent	0.2 "
Phenol sulfonic acid	7.0 "
Filler and fire retardent	2.0 "

Foaming. Mixing and foaming operations are carried out in a well-ventilated room as the fumes are objectionable to many people. If the ambient temperature is not above 70°F., heat should be supplied to the mixing pot and mold.

The components are brought to a temperature of 77°F. Resin and foaming agent are thoroughly blended. The accelerator is quickly mixed in, and the batch is immediately poured into the molds. Sometimes air is whipped

into the resin to serve as seeding nuclei for the foaming. Such foams generally have a more resilient texture but a lower compressive strength than foams made without air.⁹

Rapid foaming is essential to uniformity of texture of the foam, particularly when making a low-density foam. The reaction is exothermic, and the heat generated converts the water present into steam and also speeds the resin reaction.

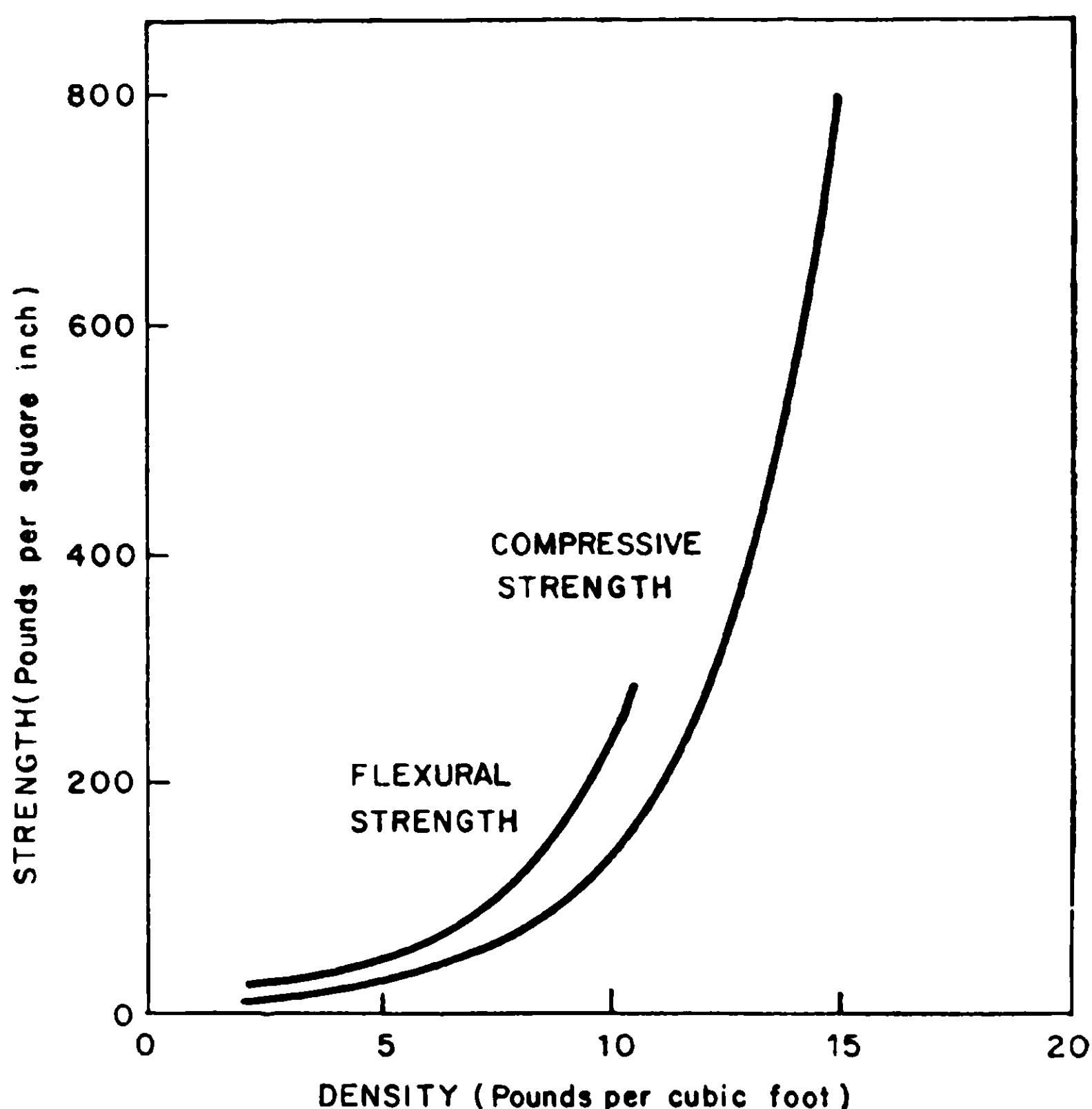


Figure 10.1. Mechanical strength versus density of foam.

In a demonstration of the process, a 4.3-cu ft cavity, 8 ft tall, was filled with phenolic foam in 55 seconds.⁴ The time from first appearance of the foam to the end was only 15 seconds. With a lighter foam that time was cut to 7 seconds.

Curing. During the foaming period the resin develops

sufficient strength to hold the foam, but it may not develop full strength for several days if it cools down to room temperature. When practical the resin is often postcured for about 18 hours at 200°F. to develop maximum physical properties.

To reduce production time when foam is made in molds, the latter are frequently held for about 15 minutes and then transferred to an oven at 140°F. for about 10 hours.

Properties. Phenolic resins have advantages over other foamed resins in cost, thermal stability, fire resistance, and adaptability to foaming in place. The distribution pattern between open and closed cells gives phenolic foams a certain amount of sound-insulation value as well as good thermal insulation.

The density of the foam can be varied from less than 1 lb per cu ft to solid resin of about 80 lb per cu ft. In Figure 10.1, data have been plotted to show the relationships between density of foam and mechanical strength. Individual formulations may show some departure from the values on the curves. Additional properties are listed in Table 10.3.

TABLE 10.3. PHENOLIC RESIN FOAMS

Heat resistance, continuous, °F.	250–500
Thermal conductivity, Btu/hr/°F./inch	0.26–0.46
Water absorption at 100% R.H., %	13–51
Sound absorption coefficient, ½-in. sheet	0.935
Shrinkage from mold, %	Appr. 0.25
Flammability	Self-extinguishing
Adhesion to wood, paper, undercoated metal	Good
Chemical resistance	Excellent except in alkalies, alcohols, and ketones
Sawing or working otherwise	With ordinary tools

Brittleness is one of the objections to phenolic foams in the low-density range. This is sometimes lessened in its effects by a tendency for the resin to develop a tougher skin on the surface. The other objection is the high water absorption.

Uses. Building and transport vehicle industries are the major outlets for rigid plastic foams at present. Phenolic resin foams have properties of interest to those industries, and prospects for the expansion of their use appear good. The more important applications are considered in the following paragraphs.

Thermal Insulation. With the growing use of plastics in building construction, increased attention is being given to the use of plastic foams for insulation. Phenolics have superior properties for that use. Best thermal insulating value is obtained on phenolic foam with a density of about 2 lb per cu ft. Goggin⁵ has estimated the material cost of phenolic foam of that density at \$0.08 per board ft as compared to \$0.10 for polystyrene and \$0.16 for urethane foam.

Phenolic foam may be used in the form of slabs or it may be foamed in place. The latter method has the advantage of completely filling the space. It also has the advantage that the foam bonds itself to the wall and does not sag. Usually a vapor-barrier sheet is required along with the foam. The adoption of foamed-in-place phenolic insulation would be helped appreciably by the development of equipment for continuous formation of foam.

Cores for Plastic Tools. The weight of cast phenolic dies and other plastic tools may be lightened by the use of foam cores. It is a relatively simple matter to mount the foam core in the mold and cast phenolic resin around it.

Sandwich Construction. Sandwich construction are important in building and transport vehicle industries. Foamed

plastic cores are one of several types of cores used and are considered by many to be the ideal core material. Phenolic resin foams have low thermal conductivity, resistance to humidity and many chemicals, good electrical properties, and controlled mechanical properties to recommend them. The combination of paper-honeycomb cores and foamed phenolic resin gives particularly good results.

Void Filler. Foamed-in-place phenolic resin offers an economical means for filling voids in ships and aircraft. A good example of its application to ships has been described.⁸ In the first application, two blister voids of a total of 230 cu ft were filled with phenolic foam having a density of 3 lb per cu ft. An examination after 2 years at sea showed no detectable change. Another installation of about 8000 cu ft cost \$55,832 for materials and labor as compared to \$225,730 for filling with the usual balsa and required 97 days less.

Packaging. Low weight per unit volume, resilience, thermal insulation quality, flame resistance, and absorptive properties are favorable qualifications for packing material. Breakage of delicate articles is reported to be substantially less.

Bakelite resin 18763 produces a foam with a density of 0.3 to 0.4 lb per cu ft and a compressive strength at 10% deformation of 0.8 to 1.2 lb per sq in. These values compare with densities of 2 to 3.5 lb per cu ft and compressive strengths of 0.4 to 0.6 lb per sq in. for shredded paper and excelsior.¹⁰ The foam is preformed as slabs which are easily cut as needed for packing.

Miscellaneous Uses. A sampling of the various applications for foamed phenolic resins is given below. These may suggest other applications.

Buoyancy materials

Decorative materials for the stage and elsewhere

Filler for cavities in plywood

Handicraft materials

Reinforcing material for rubber latex foam

Shoe lasts

Water-absorbent blocks for holding flowers and
for humidifying cigar cases, etc.

Syntactic Foams

Syntactic foams are the most recent addition to foamed resins. They are composed of microscopic, hollow phenol-formaldehyde resin spheres bonded with a phenolic, epoxy, or polyester resin into a low-density foamlike material. Production of the resin spheres is discussed in the next section of this chapter.

Densities usually lie between 10 and 40 lb per cu ft. The uncured mixture is generally a putty-like mass which can be troweled, forced into cavities, and molded. The cured product can be sawed, drilled, and painted.

Syntactic foam has one of the highest strength-to-weight ratios of all plastics. This is due to a great extent to the strength contributed by the shape of the particles. The foam also has good insulating properties.

Best potentiality for this material appears to lie in core material for sandwich construction. Another application which has possibilities is illustrated by the repair of wood parts of buildings. Rotted parts, for example, may be cut out and syntactic foam troweled in to fill the cavity.

Present cost of the resin spheres confines use of syntactic foam to aircraft applications and a few specialized uses.

SPHERES

In the normal production of plastic foams, gas is generated within a mass of resin and the whole mass is expanded. If that procedure is modified by first converting the resin

into very fine particles, each resin particle then becomes an isolated sphere, within which a bubble of gas is sealed.

Any resin can be used to make the spheres, but current production is confined to phenolic and urea resins. They range from 0.0002 to 0.005 in. in diameter with an average of about 0.0017 in. The bulk density is 3 to 5 lb per cu ft. The price quoted in published lists in late 1958 was \$0.86 per lb in truckload lots.

Production

The spheres are formed by spray-drying a mixture of resin, solvent, and either a dissolved gas or a material capable of generating the gas.¹¹ Nitrogen is commonly used as the gas. The heat in the dryer evaporates the solvent and liberates the gas. The resin dries and cures and retains the gas within it. The spheres are produced in a free-flowing condition ready for use after classifying for size.

Properties

The spheres are quite durable and can pass with liquids through pumps, valves, and pipe fittings without damage. However they can not withstand extrusion. They are damaged by pneumatic pressures in excess of 200 to 300 lb per sq in. They have floated on petroleum oils for several years without deterioration but are not satisfactory on water. They eventually sink.

The *K* factor for thermal conductivity at 5 lb per cu in. is given by the manufacturer as 0.26, which compares favorably with values for most common insulating materials. The spheres may be heated sufficiently for them to adhere without losing their low density.

Uses

These resin spheres were originally intended for floating on the surface of petroleum oils in storage tanks to reduce oil loss by evaporation. Reductions of such loss by 80 to 90% have been reported. Inspection of the spheres after 3 years in such service indicated no deterioration.

Subsequent developments led to the use of the spheres in syntactic foams as described in the preceding section. Use in various products to increase viscosity or impart opacity are possibilities. It has been suggested that they be used as fillers in acoustical tile, concrete or plaster, and dynamite. Nitrogen-filled spheres mixed with nitroglycerine make a dynamite foam that is even-burning and particularly good for oil-well and other uses.

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11. RUBBER COMPOUNDING

The properties of phenolic resins and rubbers are logical complements to each other. Not all grades of the two components are compatible and a certain amount of selection is necessary.

Rubber in small to moderate amounts improves shock and fatigue resistance of phenolic molding compounds. Phenolic resins plasticize, reinforce, and harden rubber compounds. Combinations are important in adhesives. Some phenolic resins are stabilizers for rubber compounds.

Acrylonitrile-Butadiene Copolymers

Of the various commercial rubbers, this one shows the best compatibility with phenolic resins. Properties of the rubber vary with the acrylonitrile content of the polymer. Grades used with phenolic resins are usually medium to high in acrylonitrile content.¹

Compositions with high phenolic resin content are used for molding such articles as bowling balls and mechanical and electrical parts, in which resistance to shock, vibration,

and fatigue are especially important. Compositions with approximately equal proportions of phenolic and rubber are used for such varied items as steam valve disks, storage battery boxes, and general purpose adhesives. Compositions with 10 to 25% phenolic resin and 75 to 90% rubber are used for shoe soles and other items where hardness and toughness are needed.

TABLE 11.1. PHENOLIC RESINS AS REINFORCEMENT IN NITRILE RUBBER

	No Resin or Filler	Carbon Black	Phenolic Resins*
<i>Cured 30 min. at 310°F.</i>			
Ultimate tensile strength, psi	300	2050	2550–3250
Ultimate elongation, %	40	350	300–350
Hardness, Duro A	50	65	88–95
Specific gravity	1.80	1.19	1.07–1.10
<i>Block Cured 45 min. at 310°F.</i>			
Hardness, Duro A	—	68	86–93
Compression set, ASTM Method B, %	—	12	55–84
Compression set, 70 hr. at 212°F., %	—	53	88–104
<i>Base Recipe</i>			
Hycar OR 25**		100.0	
Phenolic resin		50.0	
Zinc oxide		5.0	
Sulfur		1.5	
Benzothiazyl disulfide		1.5	
Stearic acid		1.5	

		154.5	

* Samples from five producers.

** Registered trade name of B.F. Goodrich Chemical Company, References 1 and 2.

Softening. Phenolics act as softening agents in the milling of rubber compounds. Stocks that would be very stiff if formulated with normal reinforcing pigments are easily processed.

Reinforcing. The major objective in using phenolics in nitrile compositions is to reinforce the compound. Data comparing the reinforcing properties of phenolic resins and carbon black are compared in Table 11.1. If 75 parts or more of phenolic resin is used per 100 parts of rubber, the chemical reaction between them is sufficient to cure the rubber without the addition of sulfur. With lesser amounts of phenolic resin it is sometimes possible to reduce the amount of curatives. On the other hand, even when the amount of phenolic resin is high the inclusion of sulfur and accelerators in the formulation improves the electrical properties and decreases the water absorption substantially.

Resin Proportion. As the proportion of resin to rubber is increased from 20/80 to 90/10 the following changes occur in the properties of the cured stocks:

Tensile strength	Increases from 1000 to 6000 psi
Elongation	Decreases from 450 to 2% with a sharp break at about 50%
Hardness	Increases from 31 Duro C to 83 Duro D

Styrene-Butadiene Copolymers

Phenolic resins are less compatible with this type of rubber than with the nitrile rubbers. They do not reinforce and cure the rubber. On the other hand, small proportions of resin have a strong effect on the hardness and stiffness of the cured rubber. Only 5 to 10% of phenolic resin is needed to bring the Shore A hardness up to 90 to 100.

Larger amounts of resin normally deaden the compound unless nitrile rubber is incorporated as a mutual solvent.

One part of nitrile rubber to three parts of styrene rubber is a convenient proportion. With that combination, up to 40 parts of resin can be incorporated.

Latices. Special liquid thermosetting phenolics have been developed for use with high-styrene latices. A wide range of properties can be obtained. This combination is being used for the bonding of ground cork.

Use. A major use for this phenolic resin-rubber mixture is in the production of shoe-sole stocks. It is also applicable to the production of top lifts, automobile tire beads, and other items in which hardness is desired.

Neoprene Rubber

Phenolic resins have limited compatibility with neoprene. They do assist in processing stock on the rolls by their plasticizing action, and they increase the hardness of the cured stock. The use of nitrile rubber as a common solvent for phenolic resin and neoprene has been patented.

Combinations of neoprene and phenolic resins in a methyl ethyl ketone-gasoline mixture make cements which adhere well to many materials.

Butyl Rubber

The vulcanization of butyl rubber with resole-type phenolic resin was disclosed in a 1955 patent.³ Butyl rubber-phenolic resin compounds can be vulcanized under the usual conditions of temperature and pressure. The cure rate is undesirably low for practical purposes, and various materials have been proposed as accelerators. They include metal halides, chlorinated wax, neoprene, and organic sulfonic acids.

Properties. The usual ratio of phenolic resin to rubber is about 12 to 100. Vulcanizates having tensile strengths of 2000 to 2200 psi and elongations of 280 to 700% are readily obtained on curing at 320 to 350°F. Some compositions show retention of nearly two-thirds of their original tensile strength after two weeks in circulating air at over 300°F.⁴

Vulcanizates are claimed to have somewhat better resistance to air and steam at high temperatures than the sulfur-vulcanized product.

Modification. In one modification, the butyl rubber is partially cured using approximately one part of phenolic resin per 100 of rubber. The partially cured material is then incorporated in a conventional recipe and the vulcanization is completed. If desired, petroleum hydrocarbons may be incorporated into the partially cured product. Vulcanizates are reported to have low torsional hysteresis.⁵

Uses. These compositions are used in the production of curing bags, tires, inner tubes, retreading, hose, and belting. Should the production of tires from butyl rubber increase substantially, the consumption of phenolic resins as curatives could become important. At present the use of phenolic resins for imparting properties similar to those obtained in combination with nitrile or styrene rubbers appears to be nonexistent.

Natural Rubber

The behavior of phenolic resins with natural rubbers is similar to that with styrene rubbers. Similar grades of phenolic resins are used. Selected phenolic resins are used with natural rubber in amounts up to 30 parts per 100 of rubber for the preparation of solvent cements.

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12. APPLICATIONS NOT OTHERWISE CLASSIFIED

Antioxidants and Stabilizers

Several examples are cited to indicate the trend of thought on these materials and possibly encourage further experimentation. They are not commercially important at present.

1. Reversible oxidizable and reducible resins.¹
 - (A) As polymerization inhibitors for vinyl-type monomeric material.
 - (B) As stabilizers for photographic solutions.
2. Hydrocarbon-substituted phenol-formaldehyde resin is added to a polyamide hot-melt composition to prevent oxidation of the hot melt.²
3. A dimethylphenol-butyraldehyde-formaldehyde condensate is used as antioxidant in rubber compositions.³
4. Polymers of alkyl phenols are stabilizers for soaps, oils, and rubber compositions.
5. Stabilizers for natural and synthetic rubbers include several types of phenolic condensation products, *viz.*,

- (A) Alkylated allyl phenols.
- (B) Styrene-phenol condensates formed in absence of polymerization agents.
- (C) Soluble, fusible phenol-formaldehyde resin.
- (D) Acid-catalyzed cresol-formaldehyde condensation product, prepared with excess cresol which is removed later.

Detergents

It has been proposed to prepare a detergent by condensing a phenol, which has an unsaturated hydrocarbon substituent group of 8 to 18 C atoms, with formaldehyde and then reacting with an excess of alkylene oxide.⁴

Disinfectants and Fungicides

A condensate of alkyl phenol with ethylene oxide used with a surface-active quaternary ammonium bactericide is said to produce a composition with both bactericidal and detergent properties.⁵

According to another patent, a novolak is heated in an aqueous vehicle with alkaline-earth hydroxide and sulfur until the product is soluble.⁶ The solution is said to be effective for protecting fruit from mold growth and as an insecticide on trees and shrubs. It has also been disclosed that a resinous fungicide is made by fusing a novolak with a dehydrochlorinatable polychlorinated carbocyclic hydrocarbon.⁷

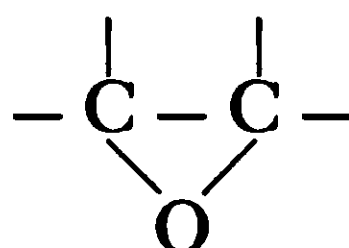
Emulsions

Emulsions can be prepared from resoles or novolaks. A solution of the resin in a water-soluble organic solvent is

dispersed in water containing polyvinyl alcohol and an emulsifying agent such as sodium oleate or an alkyl phenol-ethylene oxide reaction product. The products find use as such or in combination with pigments, softeners, soft resins, or varnish. Coatings and adhesives are the major outlets.⁸

Epoxy Resins

Epoxy resins are a young and growing type of 'thermo-setting resin. They are characterized by the presence in the resin chains of ether linkages and of reactive groups



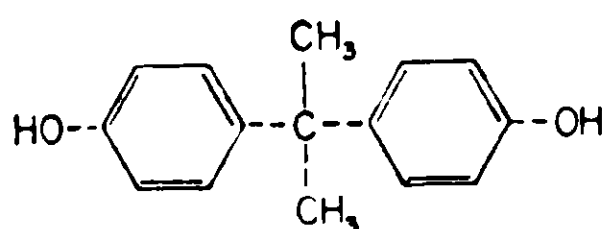
at terminal linear polymerization points. They are commonly formed by reaction of epichlorohydrin with a polyalcohol or a polyphenol.

Intermediates for Production. Numerous materials are potential starting materials for epoxy resins, but the commercially significant resins are made from glycerol, Bisphenol A, Bisphenol F, long-chain bisphenols, or novolak resins. All but one of these are closely related to phenol, but phenol itself is not satisfactory for resin production with epichlorohydrin, as the reaction products fail to harden properly.

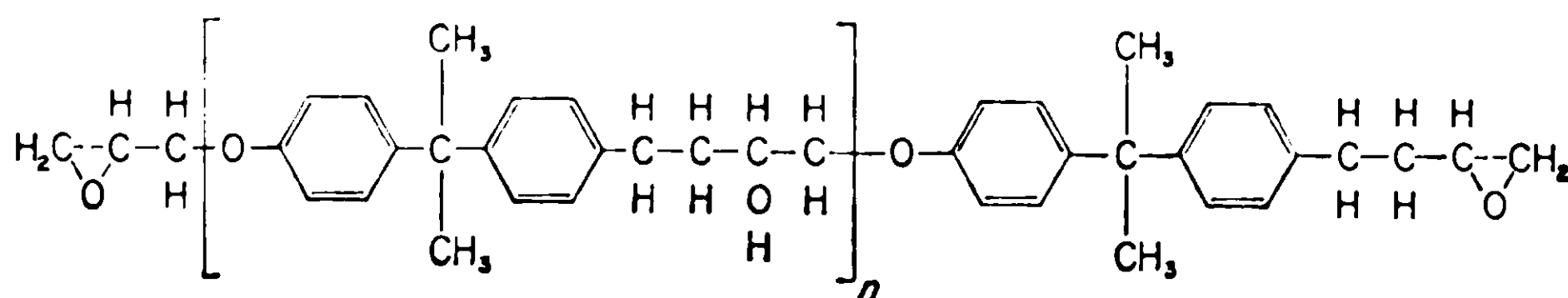
The bulk of present epoxy-resin production is made from Bisphenol A, which is an acid-catalyzed reaction product of phenol and acetone. Production of Bisphenol A in 1956 was about 25 million lb. The bulk of it went into epoxy resins and a few phenolic resins.

Novolaks. A small but growing amount of epoxy resin is made from novolak resins, which function there as polyphenols. Figure 12.1 illustrates the differences between

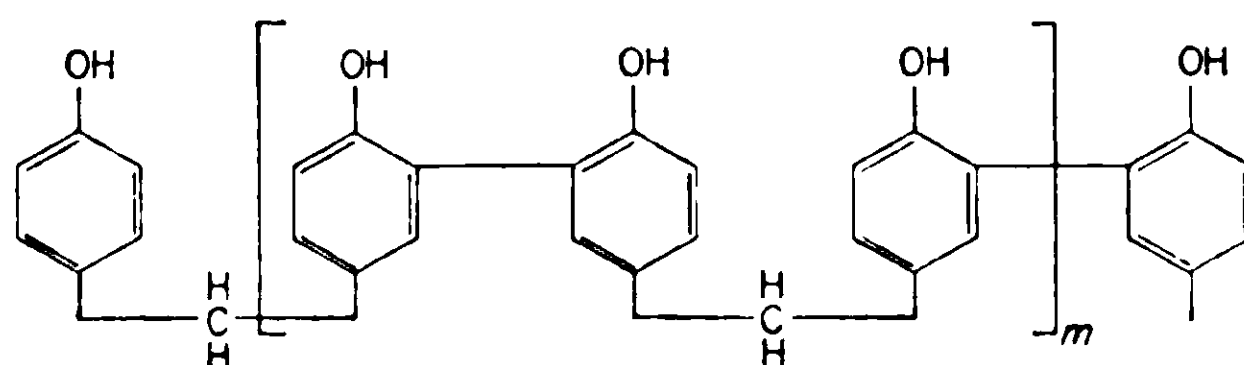
Bisphenol A and a novolak and between the epoxy resins made from them.



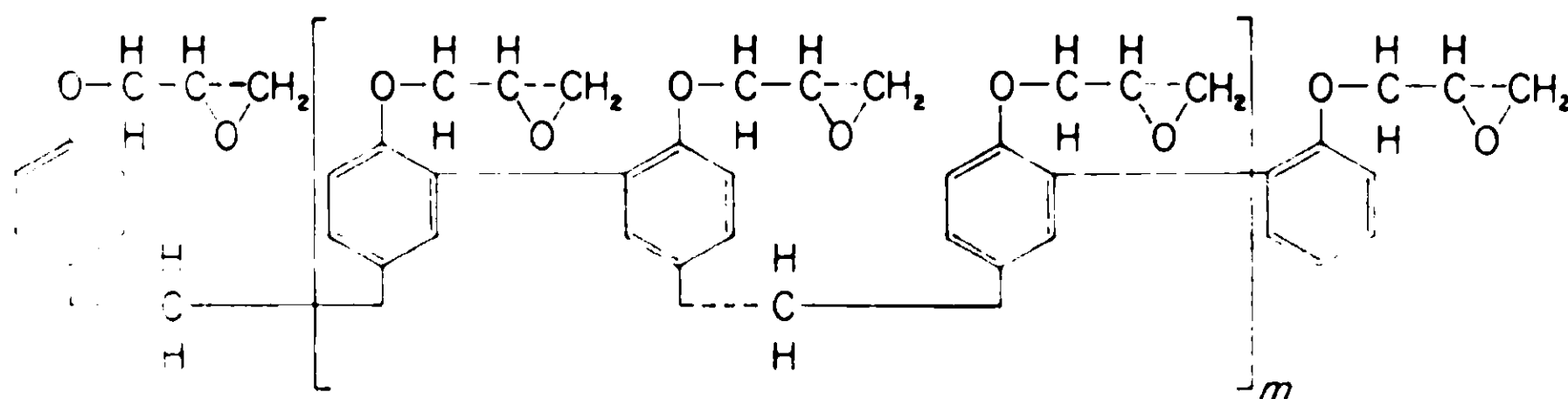
Bisphenol A (essentially a single compound)



Epoxy resin from Bisphenol A



Novolak resin, idealized form. Ortho and para positions are normally randomly occupied, and m has a variety of values.



Epoxy resin from novolak

Figure 12-1. Epoxy resins.

Initially, conventional types of novolaks were used for the production of epoxy resins. Recently, superior results have been obtained using specially prepared novolaks, and further improvements may be expected. Novolak epoxy resins may run 64°F. higher on heat distortion and 33 to 60% higher on flexural strength at 500°F. than Bisphenol

A-type epoxy. Novolak epoxy resins frequently cure faster.

Polyphenols other than novolaks may become important here. Farnham⁹ has recently disclosed the production of low-molecular weight polyphenols from an olefinic aldehyde, such as acrolein, and phenol using an acid catalyst. The product is reacted with epichlorohydrin in the same manner as a novolak.

Hardening. Phenol-formaldehyde resoles can be used to harden epoxy resins.¹⁰ The reaction is acid-catalyzed. The use of conventional resoles frequently darkens the cured resin undesirably. This is a relatively new subject, and improvements are being made. According to a recent disclosure, the phenolic hydroxyl groups of the resole are etherified before use with the epoxy resin. According to another, the resole is preferably formed by condensing a phenolate of Al, Ti, Fe, or Zn with formaldehyde.

Floors and Flooring

Phenol-formaldehyde resins are used in the production of acid-resistant floors.¹¹ Resilient tile are produced without need for a heavy-duty mixer by using a binder of rosin-modified phenolic resin, a vinyl resin, and a plasticizer.¹²

Particles of fully-cured phenolic resin molding composition are used as an abrasive in antiskid floors as on aircraft carriers. It is claimed that they do not abrade ropes or feet.¹³

Hardening Agents for Other Resins

Polyvinylals. *Meta-para-cresol-formaldehyde* condensed in the presence of ammonia or an amine has been used for years in combination with polyvinylal resin as wire coatings.

Resoles. The 3,5-xyleneol accelerates the cure of resoles.¹⁴ Color stability and other physical properties of the finished resin are said to be superior. This xyleneol also speeds the cure of resorcinol resins.

Polysiloxanes. These resins are said to be hardened by condensation products of multivalent metal phenolates and aldehydes.

Ion Exchange Resins

Phenolics were the original synthetic resin ion exchanges. Since then many other materials have come into use, and phenolics have lost their leadership. The ion exchange resins of today are practically tailor-made for a particular job.

Phenolic cation exchangers are generally prepared by introducing sulfonic acid groups into the phenol-formaldehyde condensate. Amine groups are used in place of the sulfonic groups when an anion exchange is prepared.

In general, the phenol-aldehyde reaction is carried to the gel point. The cured resin is ground, washed, dried, and sifted to proper particle size.

Uses. Phenolic cation exchangers are being used in the processing of such materials as beet sugar, fruit juice, dextrose, and wine. Some varieties have a high adsorption capacity for large organic molecules and color fractions. Their capacity rating and maximum operating temperature are lower than those of styrene-type exchangers.

Phenolic anion exchangers are used in processing beet sugar, glycerol, and pharmaceuticals and in demineralizing and deionizing water. There are special types for non-aqueous systems.

Specialty Resins. One example is Duolite S-30 of Chemical Process Company. This is a mixed polar group with

high adsorptive capacity for organic color-bodies and various polar organic molecules.

Phenolic electron exchange polymers are available which catalyze oxidation-reduction reactions. An example is Chemical Process Company's Duolite S-10. This is used to remove dissolved oxygen. In combination with selected anion and cation exchangers it purifies water for nuclear reactor systems.

Thomas and Jones¹⁵ prepare resins with arsonic acids. The resins also contain phenolic groups, preferably resorcinol, which are etherified. These resins are said to combine preferentially with ions of certain metals. Isacescu and Ursu¹⁶ treat alcohol solutions of phenol-furfural resins with mercuric or lead acetates. The modified resins have great affinity for fixation of halogens, organic halogen derivatives, and organic compounds with SH groups.

Medicinal Uses

Polyoxyalkylene ether alkanol derivatives of phenol-formaldehyde condensates are said to be of therapeutic interest in tuberculosis and in leprosy.¹⁷

The preparation of medicinal resins based on phenol-formaldehyde sulfonates has been described. They are partly in H, partly in K, and optionally partly in NH₄-form.¹⁸

Petroleum Processing

A sampling of patent disclosures is given here to illustrate the trend of thought. None have yet provided any large volume outlet for phenolics.

Drilling Mud. A sulfonated phenol-phenol-formaldehyde condensate is incorporated.¹⁹

Plugging Well Formations. Phenol-formaldehyde condensates are used alone or in combination with resorcinol-formaldehyde,²⁰ ground walnut shells,²¹ or Portland cement and liquid hydrocarbon.²²

Breaking Petroleum Emulsions. Numerous patents have disclosed the use of modified phenolic resins, such as an oxyalkylated amine-modified thermoplastic phenol-aldehyde resin.²³

Fuel Oil. The condensation product of *p*-tetramethylbutylphenol and $(\text{NH}_4)_2\text{S}$ is added to furnace oils to stabilize against oxidation and ultraviolet radiation.²⁴

Lubricating Oil. Metal and sulfur-containing alkylated phenol-formaldehyde resins are added to provide detergent and corrosion- and rust-inhibiting properties.²⁵

A neutralized reaction product of a sulfurized terpene, an alkyl phenol, and formaldehyde is added to reduce corrosion.²⁶

An oil-containing metal salt of the condensation product of a hydrocarbon-substituted phenol and a vinyl or allyl compound is included for use with high-sulfur fuels.²⁷

Small amounts of 2,6-ditertiary butyl-4-methyl phenol and a nonresinous condensation product of *para*-tetramethylbutylphenol, formaldehyde, and *N*-dimethylaniline are added to stabilize the oil.²⁸

Metal compounds of phenol-formaldehyde condensates are added to reduce engine wear and fouling.²⁹

Grease. Grease composed of 2 to 20% phenol-formaldehyde resin and 98 to 80% tricresyl phosphate or similar phosphate has been disclosed.³⁰

Asphalt. Unmodified phenol-formaldehyde is added to specified types of petroleum residuum, and the mixture is air-blown at elevated temperatures.³¹

Rockets and Fireworks

It has been suggested that phenolic resins and other resins could serve as both fuel and binder in solid propellant fuel for rockets.

Liquid phenolic resin is mixed with finely divided oxidizing agent plus the desired coloring material. The resin is then polymerized to give a pyrotechnic mass.³²

Soil Stabilization

Various attempts have been made to use phenolic resins. Phenol-furfural resins gave poor results. Phenol-formaldehyde resins were better but were still not successful. Best results were obtained with resorcinol-formaldehyde resins. Using about 5% of resin on the soil, a hard water-repellent mass was obtained in a few days.³³

Tanning Agents

A substantial group of synthetic materials have made a place for themselves in the tanning of leather, since their introduction in about 1920. The commercially important syntans are condensation products of formaldehyde with a naphthalene sulfonic acid, a phenol, a sulfonated phenol, one of the urea-melamine family, or some types of sulfones. A few syntans are produced without formaldehyde.

Production. Production of syntans in 1956 was approximately 35 million lb, of which 26 million lb were naphthalene derivatives, and approximately 9 million lb included all other types. Average unit values of the two groups, according to the Tariff Commission, were \$0.16 and \$0.22 per lb, respectively. To be competitive, syntans must be relatively inexpensive. The price differential between the

two above groups makes one strong explanation for the greater volume of production of the naphthalene types.

Authoritative data are not available, but it is estimated that the production of phenolic products was approximately 4 million lb, divided among approximately six major producers. There may be captive production in small amount.

Use. Some of the syntans, particularly the phenolic types, may be used as the sole tanning agent, even on heavy leather. The more general practice, however, is to use them in combination with some other tanning agent. In combination with vegetable tannage, a syntan may be used to reduce the astringent action of the vegetable material and thus permit better penetration, as a dispersing agent for the vegetable material or as a pretannage. In combination with chrome tannage, syntans may be used as a pretannage, as a bleach for lighter-colored leather, to assist the dyeing of the leather, or as a dispersing agent for some other treatment.

In addition to tanning, some of the syntans have a filling or plumping effect on the leather. A short summary of some of the relationships between phenolic-type syntans and performance follows:

	Tanning	Filling
Formaldehyde condensation product of sulfonated phenols	Good	Poor
Formaldehyde condensation product of mixture of sulfonated and unsulfonated phenols	Better	Poor
Sulfonated product of phenol-formaldehyde condensation	Better	Better
Formaldehyde condensation product with a polyphenol	Very good	Very good

Textile Fibers

Fiber-Forming. Little advance has been made in the use of phenolic resins for the production of fibers. The most

interesting approach appears to be the condensation of phenol-formaldehyde condensate with a polyamide.³⁴

Pohl³⁵ included phenol-formaldehyde in his studies on reaction-spinning of fibers, in which the fiber hardens by chemical reaction after it leaves the spinneret.

Textile Treatments. Patents directed to improved crease resistance or shrink-proofing of textiles frequently mention phenol-formaldehyde resins among others. In general, phenolic resins cannot compete with urea resins in this field. This is because of the cost, ease of application, and performance of the latter.

Bell and co-workers³⁶ have shown that halogenated phenolic resins are more efficient than phenol-formaldehyde as rotproof finish for viscose rayon yarn.

Resorcinol resins are among the materials used for the treatment of fibers to improve the bond between the fibers and the rubber in automobile tires.³⁷

Coatings. An interesting coating for fabrics is disclosed by Fay.³⁸ The fabric is coated with a solution of a butadiene acrylonitrile copolymer and a novolak resin. Then a coating of the copolymer is applied by calendering. This type of fabric is used for upholstery. A modification of this process is used to prepare felts for paper machinery and the like.³⁹

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13. PROSPECTS

Phenolic resins have a very attractive combination of properties, versatility, and price structure. As Landall has said, they are “first of the modern plastics in time and first in value.” They are well-established in a wide variety of industries. There appears to be agreement that the present consumption pattern will continue for the next several years. This is very probably a minimum since there is reason for optimism as to increased consumption and wider application.

Substantial improvements have been made in phenolic resins over the years since their introduction. In spite of that, the full potentialities of these resins are not being realized today. It is only quite recently that we can see evidence of what really can be done with phenolics and hints of further possibilities. A brief review of phenolic resin development may help to clarify the present status.

Phenolic resins were introduced at a time when research-and-development laboratories were not as numerous or as well staffed as at present. The chemistry and mechanisms of resin formation were incompletely understood. Methods

adopted for production were basically of the cookbook variety. Such laboratory facilities as were available for work on phenolics were kept busy with production problems and with customer service in connection with extension of resin applications.

Next came a period of substantial growth of the plastics industry. This brought new resins competitive with phenolics and an increase in the number of producers of phenolic resins. Better laboratories were available, but there was also more demand upon them on day-to-day problems of cost reduction, meeting the performance of competitive phenolics, investigating new resins that threatened phenolics, and tailoring resinous products to customer demands. Little manpower was available for fundamental studies of phenolics.

Phenolic resin prices were driven down by competition to a level where the margin of profit became so slim that many manufacturers lost enthusiasm for research and development beyond the barest minimum. By this time a number of researchers were inclined to pass up phenolic resins as "old stuff" and apparently held the erroneous impression that everything worthwhile was already known about phenolics.

Fortunately there have been notable exceptions to that research attitude. Bender and other workers have done a great deal to put phenolic resins on a sounder technical basis. Their publications in recent years have undoubtedly increased interest in phenolics. Considerable information on the fundamentals of phenolic resins has come from abroad and in particular from Japan and Russia.

The demands of the aircraft and missile programs for plastics of specific properties have provided an incentive for a break-through in phenolic resin development. We now have reinforced phenolics with resistance to heat

greatly superior to that of any previous types. We have resins that cure up to 70% faster than before. We have phenolic resin alloys of superior performance as adhesives. The value of some of these new resins is indicated by the fact that they are selling at prices in dollars per pound. Only a few years ago the suggestion of such a price would have seemed preposterous.

Faster-curing phenolic molding compounds plus automatic molding equipment make the molding of thermosetting phenolics more competitive with injection molding of thermoplastics. The use of certain resin alloys allows phenolics to be molded in a range of colors. Many articles now molded from thermoplastics would be better if molded from thermosets. These improvements in phenolics may help them to get some of that business.

If these improvements are promoted properly they should lead to a marked increase in phenolic resin consumption. It is admitted that current prices of many of the newer resins are too high for other than specialized applications. However, as consumption increases and the resins move into larger volume production this should be corrected.

Like all synthetic resins, phenolics have their shortcomings. For example, they are not fashionable as to color, and they are criticized because in the majority of cases they require pressure and a relatively high temperature to cure them. Some work has been done on the control of color, but the real answer has not been found. As to cure, it seems highly improbable that all avenues of approach to low temperature cure of phenol-formaldehyde condensates have been explored. A break-through on that would be highly profitable. It would enlarge the scope of wood lamination, adhesive and other bonding, coatings, and reinforced plastics especially.

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